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in the Madison and Missouri Rivers**

Report No. 180B

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**Processes Affecting Arsenic Transport
in the Madison and Missouri Rivers**

Report No. 180B

by

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Final Technical Report Submitted to
The Montana Water Resources Center
Montana State University
Bozeman, Montana

1992

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The following thesis fulfills the Section 104 research program reporting requirements for J. L. Sonderegger during the time period of April 1, 1991 through March 31, 1992.

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Jon Schulman

MOBILITY AND TRANSPORT OF ARSENIC
IN THE MADISON AND MISSOURI
RIVER BASINS OF MONTANA

by
Jon Schulman

A thesis submitted to the
Department of Environmental Engineering
Montana College of Mineral Science and Technology
in partial fulfillment of the requirements for the degree of
Master of Science in Environmental Engineering

Montana College of Mineral Science and Technology

Butte, Montana 59701

December, 1992

Abstract

High concentrations of arsenic in the Madison and the upper Missouri Rivers in Montana emanate from geothermal sources in Yellowstone National Park. Concentrations seventy times higher than the EPA drinking water standard have been reported in the headwaters. This study was funded by the Montana Water Resources Research Center and the Montana State Water Quality Bureau to help determine the behavior of arsenic as it travels through this system.

The study found the major influence on arsenic concentration is dilution as it travels downstream. In the main river, particulate phase arsenic remains small compared to dissolved phase, and dissolved arsenic(V) species dominate dissolved arsenic(III) species.

Because the study was conducted over a four month period it was inadequate to determine if Canyon Ferry Reservoir, which has an average residence time of almost seven months, is acting as a sink for particulate phase arsenic. However, the available data suggest that sedimentation is occurring in the reservoir.

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Introduction

Arsenic concentrations more than thirty times the EPA's drinking water standard (50 ug As/l [micrograms arsenic per liter]) are discharged into the headwaters of the Madison River by geothermal springs in Yellowstone National Park. Through dilution and sedimentation the arsenic concentration is reduced to approximately the drinking water standard at the mouth of the Madison River, which is the beginning of the Missouri River. Concentrations remain seasonally above the US Public Health Service's recommended drinking water standards (10 ug/l) for at least 200 additional miles downstream, past the cities of Helena and Great Falls, which use Missouri River water as all or part of their municipal water supplies. Research has also shown that ground water along the rivers has become contaminated through the use of arsenic laden river water for irrigation (Sonderegger and Sholes, 1989).

Funded by the Montana Water Quality Bureau and the Montana Water Resources Research Center, this study was designed to provide additional information on the mobility and transport of arsenic in the Madison and Missouri river basins. More specifically, it was designed to improve current understanding of the partitioning of arsenic from the dissolved phase to the particulate phase between Ennis and Great Falls (the study area), and to determine if particulate arsenic is settling out of the water column and

accumulating in the sediments along this same reach of the rivers.

Background

1. Yellowstone Park

A dome of molten rock a mile or two below the surface of Yellowstone National Park heats water to temperatures in excess of 240 °C (465 °F) under high pressure. This superheated water drives the thousands of geothermal features for which the park is famous. As the superheated water forces its way to the surface it dissolves minerals in the rock layers between the deep magma chamber and the surface, carrying the dissolved minerals with it (Keefer, 1976).

Most minerals are more soluble in warm water than they are in cool water. Consequently, water from geothermal sources tends to carry higher concentrations of minerals than groundwater springs or surface sources. For example, natural arsenolite, As_2O_3 , has a solubility of 1.2 grams per 100 cc of water at 2 °C, but will dissolve 11.46 grams per 100 cc of water at 100 °C, under similar pressures (Weast et al., 1965).

The rapid cooling of the water when it reaches the surface reduces the solubility of many minerals to the extent that the solution becomes supersaturated at surface temperatures and pressures causing minerals to be deposit

ed from the solution. Thus the surface area around individual geothermal features is often built up with large mineral deposits (Keefer, 1976).

The specific species carried by the water depend on the rock through which the water travels. At Mammoth Hot Springs, where the underlying rock is limestone, travertine is the dominant precipitate at the surface. In all other major geothermal areas of the Park, the dominant surficial deposit is siliceous sinter (also called geyserite; Keefer, 1976). Table 1 is an analysis of the precipitates from Mammoth Hot Springs and the Upper Geyser Basin. The former drains into the Yellowstone River and the latter drains into the Madison River.

Water from the Upper and Lower Geyser Basins and from Norris Geyser Basin feed the Firehole and the Gibbon rivers, respectively. These, in turn, form the Madison River. Table 2 gives water analyses of two hot springs and the Firehole, Gibbon and Madison Rivers in Yellowstone Park. The map in Figure 1 gives the sampling sites for Table 2 (Stauffer et al., 1980). Seventy to seventy-five percent of the water at site #3 is from the Firehole River and the remainder is from the Gibbon River. The analysis shows slight losses of arsenic, iron and fluoride, but declining concentrations of manganese and aluminum. This indicates that the water had not reached equilibrium, yet the arsenic and fluoride concentrations appeared to be relatively stable; fluoride

Table 1

Analyses of Some Precipitates
(Composition Given in Percent by Weight)

Constituent	Travertine, Mammoth Hot Springs	Geyserite, Upper Basin
SiO ₂	0.09	72.25
Al ₂ O ₃	0.055	10.96
Fe ₂ O ₃	0.055	0.76
FeO	n.d.	0.31
MnO	n.d.	n.d.
MgO	0.35	0.1
CaO	55.37	0.74
Na ₂ O	n.d.	3.55
K ₂ O	0.04	1.66
NaCl	0.1	0.36
SO ₃	0.44	0.45
CO ₂	43.11	n.d.
C	n.d.	0.2
TiO ₂	n.d.	n.d.
P ₂ O ₅	n.d.	n.d.
H ₂ O	0.32	9.02
C. organic	0.17	n.d.

Total	100.1	100.36

Source: Rankama and Sahama, 1950

Table 2

Chemical and physical parameters of selected sites.
(samples filtered)

Parameters	Sites						
	A	B	1	2	3	4	5
Temp (C)	83	89	15	14	18.5	18.5	16.5
pH	7.78	7.49	8.4	7.04	7.5	7.68	8.25
Eh (mV)	18	-76	452	402	358	394	448
O ₂ , aq (mg/l)	0.92	0	7.6	9.1	8.4	8.15	8.2
Alkalinity (mg/l)	340		106	115	115	108	109
Na (mg/l)	307	311	73.6	55.4	68.1	67.5	66.4
K (mg/l)	15.2	13.4	6.75	8.4	7.25	7.15	7.15
Li (mg/l)	3.42	2.93	0.528	0.323	0.477	0.457	0.450
Mg (mg/l)	0.009	0.079	0.483	1.23	0.704	0.691	0.762
Ca (mg/l)	0.54	2.1	5.24	8.29	6.37	6.04	6.12
SO ₄ (mg/l)	21	50	10	18	13	12	12
Cl (mg/l)	262	310	54	33	47	45	44
F (mg/l)	22	28.6	7.2	4.1	6.4	6.4	6.3
SiO ₂ (mg/l)	270		100	75	92	86	87
S (ug/l)	<15						
Al (ug/l)	41	69	52	235	111	97	90
Fe (ug/l)	2.8	17	14	30	16	13	14
Mn (ug/l)	3	7.7	2.6	24	7.6	5.8	1.6
As(V) (ug/l)	1380	30	245	92		185	
As(V)+As(III) (ug/l)	1455	1420	252	83	212	200	204
Sb (ug/l)	58	73					
P (sol/react) (ug/l)	2	2	6	4	6	8	2

A. Octopus Spring

B. Azure Spring

1. Firehole River (see "1" on map for location)

2. Gibbon River (see "2" on map for location)

3,4,5. Madison River (see "3" on map for location)

from Stauffer et al., 1980

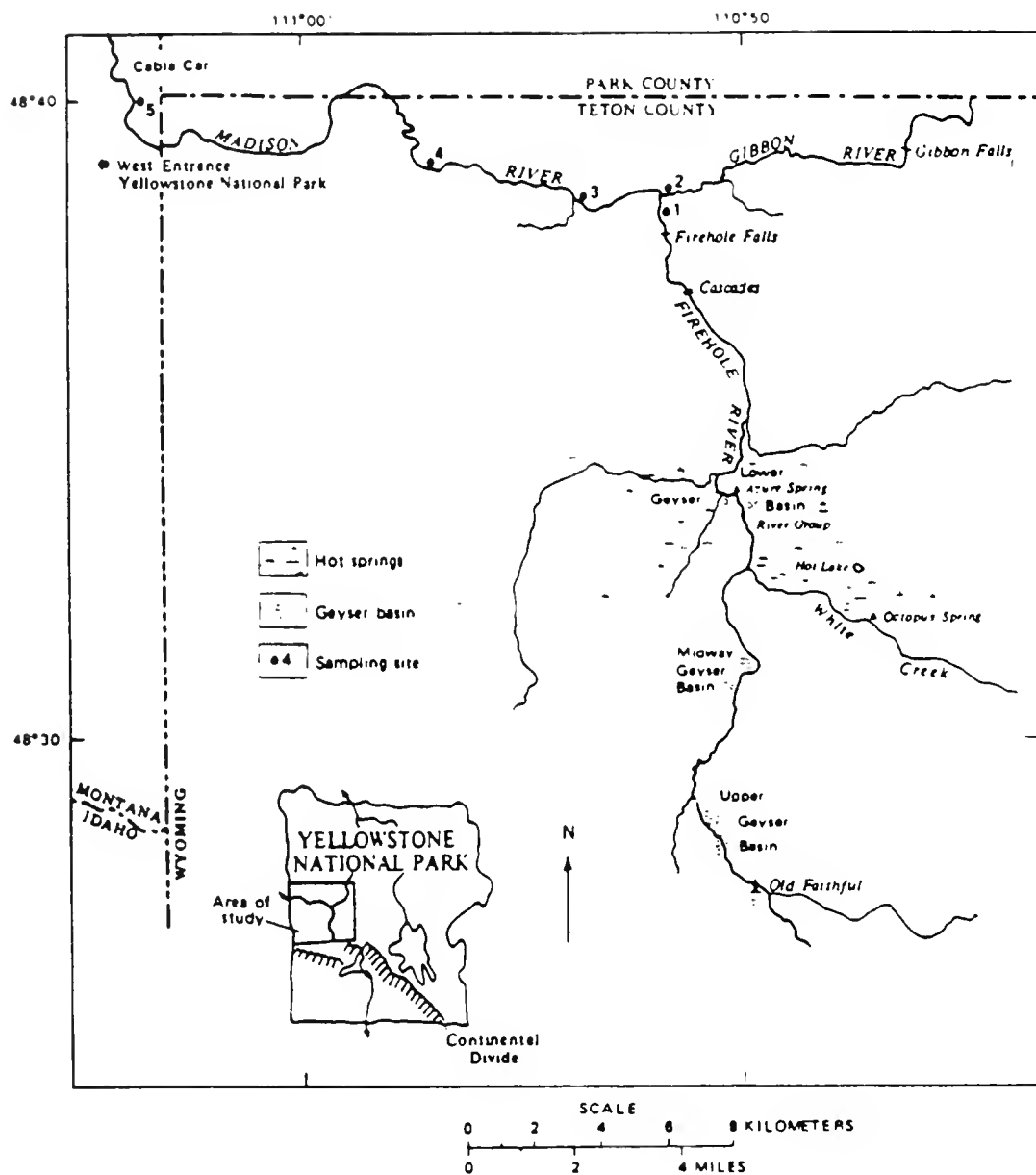


Figure 1. Sketch map showing rivers and major hydrothermal areas sampled in Yellowstone National Park, Wyoming.

from Stauffer, 1980

is a "standard" indicator of chemical conservatism. Iron is the ion often most responsible for causing the precipitation or adsorption of arsenic; its concentration (13-16 ug/l) and apparent stability in these headwaters will be noted again in this thesis.

Total arsenic concentrations exceeding 3500 ug/l have been reported in geothermal waters in this system (Stauffer and Thompson, 1984). Micrograms-per-liter approximate parts-per-billion in dilute solutions such as these.

2. EPA Drinking Water Standard

The U.S. Environmental Protection Agency has set a Maximum Contaminant Level (MCL) of 50 ug/l for arsenic in municipal drinking water supplies (USEPA, 1980). This standard is based on the assumption that most people consume about two liters of tap water per day.

Although the standard is based on a concentration, it is often easier to judge conservatism when the concentration and the stream flow are merged to provide the total mass loading of arsenic passing a given point in a river. As uncontaminated tributaries enter the river, or water evaporates from it, the arsenic concentration should fall or rise (respectively) in proportion to the dilution or concentration, yet the net amount of arsenic in the river may remain

unchanged. Thus, both concentration and mass flux are important indicators of different processes occurring during the downstream transport of the contaminant. For this reason, both measures will be used in this paper.

The U.S. Public Health Service recommends a maximum arsenic level of 10 ug/l in drinking water, which is not binding (Mok, 1988). In recent years the EPA has proposed changing the MCL for arsenic to 20 ug/l, but has not changed the standard as of this writing (Horpestad, 1992).

At the current standard for arsenic (50 ug/l), the Madison River does not usually meet federal drinking water standards, and, at times, the Missouri River above Canyon Ferry Reservoir exceeds the limit as well (USGS, 1991). This precludes full-time use of untreated water as a municipal supply for West Yellowstone, Ennis, Three Forks and Townsend.

Furthermore, should the EPA lower its maximum contaminant limit for drinking water to 10 ug-As/l, neither Helena nor Great Falls could use Missouri River water as their municipal sources without first reducing the levels of arsenic in water withdrawn from the river. Currently, Great Falls gets all of its drinking water from the Missouri River, and Helena uses the Missouri as a secondary water source.

3. This Study

If it becomes necessary to remove arsenic from Missouri River water, it will be important to know what chemical and physical forms the contaminant takes as it moves downstream so that the most efficient, cost-effective treatment may be applied. For example, dissolved species are, by definition, comprised of particles smaller than 0.45 μm (micrometers) in diameter. Particles of this size are difficult to remove by simple filtration; instead, a chemical or ion exchange process may be required. During spring runoff and other high water events, rivers carry increased quantities of suspended particles ($>0.45 \mu\text{m}$ in diameter), causing contaminants which are normally found predominantly in the sediments to become entrained into the water column.

Water use is not limited to municipal supply. Applications to withdraw water from the Madison River for irrigation are pending, and new applications continue for agricultural, industrial and other uses. This study is an outgrowth of research which found arsenic concentrations in the ground water in the lower Madison valley at concentrations up to three times as high as those found in the adjacent river. This phenomenon is believed to be the result of a century of irrigation with contaminated river water in the valley (Sonderegger and Sholes, 1989).

This study is aimed at closing some of the gaps in existing information about the mobility and transport of

arsenic in the Madison River and the upper Missouri River drainages. Current and future uses of the river can then be managed more effectively.

4. Arsenic

The toxicity of arsenic is well documented and requires no further reference (USEPA, 1980). On the other hand the relative toxicity of the different natural compounds of arsenic is of interest, and the complex nature of arsenic is essential to understanding this study's findings.

As the abbreviated periodic chart (Figure 2) shows, arsenic is the thirty-third element, found in Group V, and, technically, a non-metal. It is sometimes referred to as a "metalloid" because it often behaves like a metal. Inorganic arsenic occurs in four oxidation states; -3, 0, +3 (III) and +5 (V). Arsenic can also be reacted biologically to produce organic forms, notably methylated. In other words, arsenic has traits similar to those of its neighbors in the periodic chart, especially phosphorous and sulfur.

Table 3 shows some common compounds of arsenic. Studies have shown trivalent (+3) arsenite to be about ten times more toxic than pentavalent (+5) arsenate, and about thirty-five times more toxic than organic forms, such as methylarsenate. The most toxic form is arsine (AsH_3) (Faust and Aly, 1981; USEPA, 1980).

Figure 2

IV		V		VI	
7	2, 4, 0, -4	8	1, 2, 3, 4, 5, 0, -1, -2, -3	9	-2
C	Carbon	N	Nitrogen	O	Oxygen
12.011		14.007		15.999	
14	2, 4, 0, -4	15	3, 5, 0, -3	16	4, 6, 0, -2
Si	Silicon	P	Phosphorus	S	Sulfur
28.086		30.974		32.064	
32	2, 4, 0	33	3, 5, 0, -3	34	4, 6, 0, -2
Ge	Germanium	As	Arsenic	Se	Selenium
72.59		74.922		78.96	
50	2, 4, 0	51	3, 5, 0, -3	52	4, 6, 0, -2
Sn	Tin	Sb	Antimony	Te	Tellurium
118.69		121.75		127.60	

Table 3-Common Compounds of Arsenic

<u>Species</u>	<u>Name</u>	<u>Oxidation State</u>
H_3AsO_4	Arsenic Acid	+5
AsO_4^{-3}	Arsenate	+5
H_3AsO_3	Arsenous Acid	+3
AsO_3^{-3}	Arsenite	+3
$\text{CH}_3\text{AsO}(\text{CH})_2$	Monomethyl Arsonic Acid	+3
$(\text{CH}_3)_2\text{AsOOH}$	Dimethyl Arsinic Acid	+1
AsH_3	Arsine	-3
FeAsS	Arsenopyrite	
As_4O_6	Arsenolite	+3
$\text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	Copper Arsenate	+5
$\text{Cu}(\text{AsO}_2)_2, \text{CuHAsO}_3$	Cupric Arsenite	+3
$\text{Fe}_3(\text{As})_4 \cdot 6\text{H}_2\text{O}$	Iron Arsenate	+5
PbHAsO_4 & $\text{Pb}_3(\text{AsO}_4)_2$	Lead Arsenate	+5
MnHAsO_4	Manganese Arsenate	+5
As_2S_3	Orpiment	+3
As_4S_4	Realgar	

Many toxics, such as PCB's and cyanide, can be removed from the environment by decomposing their molecules into component molecules or elements. Because arsenic is an element, removal by decomposition is not possible, so arsenic is said to be conservative.

Arsenic is often a contaminant resulting from mining activity and acid mine drainage, which produces conditions quite different from those found in the study area. Some of the research on arsenic under acid mine drainage conditions is included in the literature review section, but, for the most part, this paper will concentrate on the behavior of arsenic under the conditions found in the study area.

In natural, uncontaminated surface water, dissolved arsenic is predominantly found as species of arsenous acid and arsenic acid (Fig 3; USEPA, 1987). As the figure shows, under the oxidizing conditions and higher pH normally found in uncontaminated surface water, dissociated species of pentavalent arsenic acid dominate. But, like many elements in the natural environment, arsenic can be cycled through several states as it works its way downstream. Figure 4 shows the complex interactions between arsenic and its environment which may result from changes in pH, oxidation potential, sorption and biological activity (USEPA, 1987).

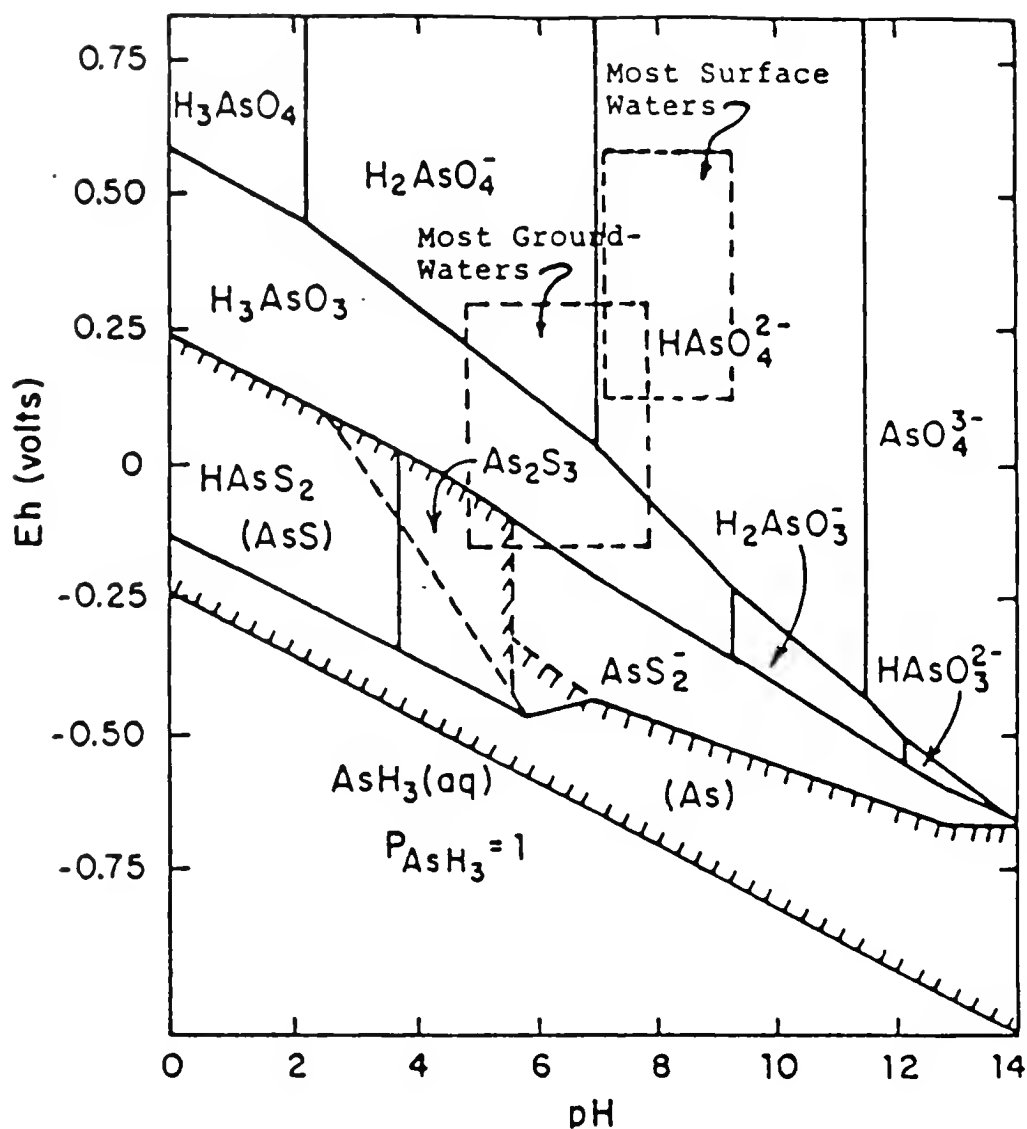


Figure 3. The Eh-pH diagram for As at 25°C and one atmosphere with total arsenic 10^{-5} mol/liter and total sulfur 10^{-3} mol/liter. Solid species are inclosed in parentheses in cross-hatched area, which indicates solubility less than $10^{-5.5}$ mol/liter.

from U.S.E.P.A., 1987

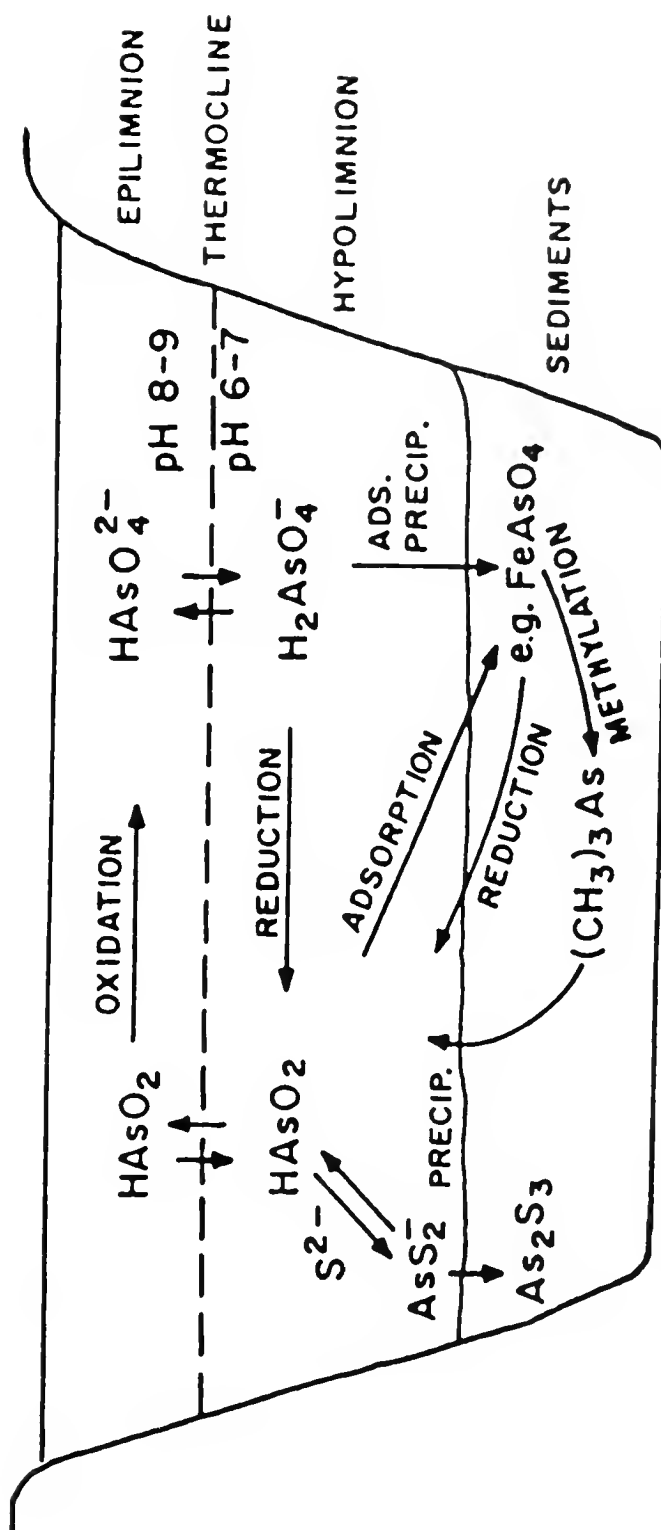


Figure 4. Stratified Lake Cycle for arsenic from U.S.E.P.A., 1987

Using Figure 3 again, in well oxygenated water, with an oxidation potential of 200-600 millivolts and a pH of 7-9, HAsO_4^{2-} will be the dominant form of dissolved arsenic. It is important to note that, although the arsenic ion in this molecule has a valence of +5, the molecule is anionic (-2) and not a cation. The arsenic-oxygen bond is so strong that, in oxygenated water, arsenic is unlikely to be found as a free, elemental cation.

One way this anion can be transformed is through physical adsorption onto other species. Arsenic's affinity for iron oxides is well documented (Pierce and Moore, 1982; Belzile and Tessier, 1990). Hydrous iron oxides and arsenate can also coprecipitate to form the mineral scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) (Mok, 1988). Arsenic also adsorbs onto manganese oxides, clays and other compounds of low solubility which tend to settle out in slow sections of rivers, or in lakes and reservoirs, where it can stay in the sediments for indefinite periods of time. In river sediments the next high water event may entrain particles back into the water column as suspended arsenic until the next quiescent reach of water causes them to resettle.

Several other scenarios for particulate phase arsenic are common. Plants, bacteria and other organisms take up inorganic arsenic compounds and convert them into organic forms, most commonly through combination with methyl ions (methylation). Studies indicate that when organic com-

pounds are liberated from organisms arsenic reverts relatively quickly to arsenite and then arsenate (MT DNRC, 1991).

If the sediments are anaerobic, arsenate can be reduced to arsenite. Some reduced forms are more soluble than their oxidized counterparts. In the case of arsenic adsorbed onto oxides of iron, for example, this can lead to the cycling of arsenic back into the water column, because of arsenite's lower affinity for adsorption onto oxides of iron, and its higher solubility once it is desorbed (Mok, 1992).

Sediments which become buried with time can experience a similar cycle. After the adsorbed arsenate is buried, it can be reduced to arsenite, desorbed, dissolved in the interstitial water, and finally diffused up through the sediments and back into the water column.

Arsenic can also form insoluble sulfides, or react with cations to form insoluble compounds (Moore et al., 1988). In either case, assuming no substantial shifts in solution pH, the arsenic will remain bound indefinitely, working its way downstream, becoming buried in the sediments, or being taken up by organisms. Some compounds of arsenic may be removed from solution through volatilization as well. Both of these scenarios are less important than the adsorption and coprecipitation models in natural conditions similar to those found in the study area (MT DNRC, 1991).

To date, arsenic research in the study area has not included analysis of suspended sediment for arsenic, or analyzed arsenic for oxidation state (redox). USGS studies have included both total arsenic and dissolved arsenic concentrations, the difference being, theoretically, particulate phase arsenic (U.S.G.S., 1976-91). But, perhaps because of differences in analytical methodology between the two classifications, this approach has some drawbacks. For example, in both the current study and the USGS studies there are several occasions where the concentration of total arsenic (dissolved plus suspended) is reported to be lower than that of the dissolved fraction alone--an obvious contradiction. Further discussion in the experimental procedure section expands on the difficulty of this analysis.

Sediment and redox analysis can provide important insights into the behavior of arsenic in the study area. If, for example, there is a significant rise in the ratio of particulate phase to dissolved phase at one of the sampling sites, it may be that the rise in the particulate fraction is a result of sediments from upstream being entrained into the water column by a scouring event, or that an upstream source (or tributary) is adding clays, iron oxides or other compounds which sorb arsenic, or that a source of particulate phase arsenic is entering upstream of the site.

Similarly, assuming no significant drop in pH or oxidation potential, an increased ratio of arsenic (III) to

arsenic (V) implies either a new source of arsenic from an underground source or re-entrainment of arsenic from a reducing environment (i.e. sediments or an organic source). Any of the above scenarios might affect the way in which the arsenic may need to be regarded.

5. Study Area - General

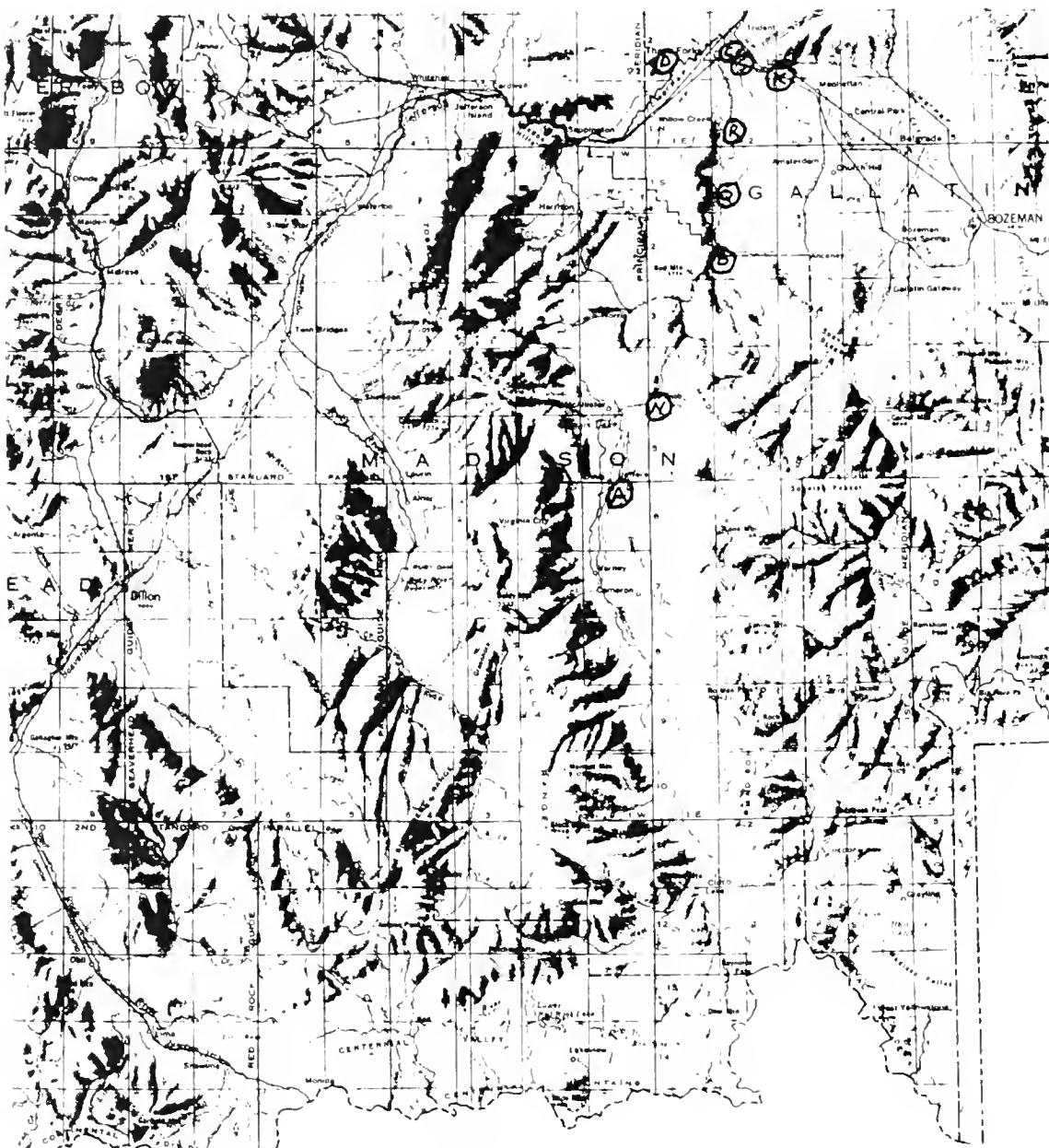
The Missouri River begins at the confluence of the Madison, Jefferson and Gallatin rivers near Three Forks, Montana. The site was named "the essential point in the geography of this west part of the continent" by Captains Meriwether Lewis and William Clark in 1805 (Newby, 1988).

Because the Madison River contributes several times as much arsenic to the Missouri River as either the Jefferson or the Gallatin River, the latter two are treated as tributaries of the Madison for the purposes of this study. Sampling for this study began at Ennis and proceeded downstream to Morony Dam, below Great Falls, Montana. This report includes the findings of previous studies from the headwaters in Yellowstone National Park through Great Falls. Figures 5 and 6 show the Madison River and the upper Missouri River, respectively.

"Major" towns (by Montana standards) along the Madison and Missouri rivers in the study area are as follows (U.S. Dept. of Commerce, 1991; MT DNRC, 1991):

Figure 5. Madison River

from Yellowstone National Park to confluence with the
Jefferson and Gallatin rivers

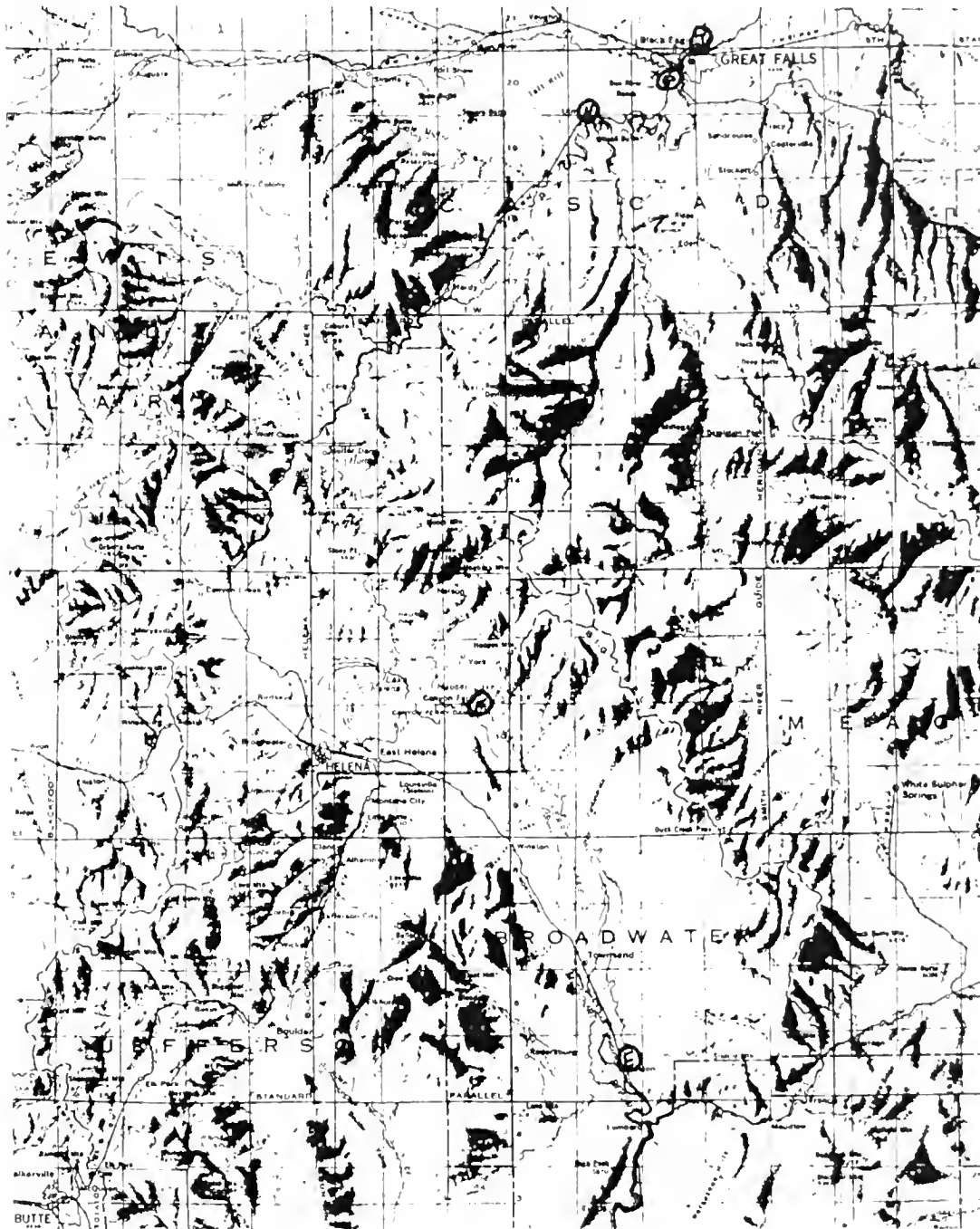


Sampling Sites: A. Ennis, Mt., B. Black's Ford, C. Madison River at Highway 10, D. Jefferson River, K. Gallatin River at Logan, N. Below Ennis Dam, Q. Greycliff, R. Cobblestone, S. Irrigation Return.

USGS Base map w/shaded relief, State of Montana, 1"=16 miles

Figure 6. Upper Missouri River

from the confluence of the Madison, Gallatin and Jefferson rivers to Morony Dam



Sampling Sites: E. Toston, F. below Canyon Ferry Dam, G. Sun River, H. Missouri River at Ulm, J. below Morony Dam.

USGS Base map w/shaded relief, State of Montana, 1"=16 miles

<u>River Mile</u>	<u>Town</u>	<u>Population</u>	<u>Elevation</u>
133	West Yellowstone	900	6650 ft
51	Ennis	800	4950 ft
4	Three Forks	1200	4061 ft
-42	Townsend	1600	3813 ft
-94	Helena	24,600	3650 ft
-200	Great Falls	55,100	3312 ft

For the purpose of this study, river mile 0 is the mouth of the Madison River (the beginning of the Missouri), and the upstream direction is positive.

Figure 7 shows water consumption for the Madison, Jefferson and Gallatin rivers, and Figure 8 shows the same for the Missouri River above Morony Dam (MT DNRC, 1991). In each case, irrigation represents the majority of the water consumed through its course, with evaporation from reservoirs constituting a significant source of water loss in the study area.

Study Area - Hydrology

The Madison River is well-known among fishermen for the high quality of its water. Exclusive trout fishing lodges are among the few signs of civilization between Ennis and West Yellowstone. Trout are an indicator species of water quality because of their low tolerance for less than pristine water.

Figure 7
Water Consumption, Headwaters

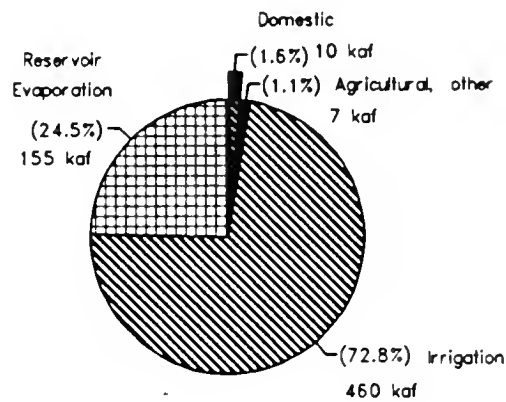
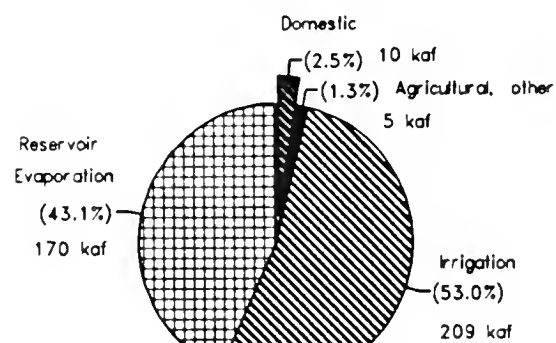


Figure 8
Water Consumption, Upper Missouri



kaf = 1,000 acre-feet per year
Source: Montana DNRC, 1991

Appendix B gives a river mile accounting of elevation, drainage area, reservoirs and incoming tributaries from West Yellowstone to Morony Dam. Figures 9 and 10 summarize this information.

Figure 9 shows how the steep slope of the headwaters is gradually reduced until, by Great Falls, the slope of the river system is almost as flat as that of the reservoirs. Below Great Falls the Missouri falls quickly through the five electric generating dams which harness the falls for which the city is named. The slopes shown by this graph relate directly to the velocity of the water, which, in turn, relates directly to the rate of sedimentation.

Figure 10 shows, by larger (vertical) increases in the drainage area, where major tributaries enter the rivers, the most obvious being the confluence of the Madison with the Jefferson and the Gallatin. These inputs relate directly to increases in overall stream discharge and dilution of arsenic (assuming that the tributaries do not also introduce high concentrations of arsenic). Because precipitation rates may vary over a drainage, a linear relationship between drainage area and stream discharge should not be assumed.

Table 4 gives an indication of the increasing discharge through the study area, as well as the volumes of the reservoirs relative to the flow through them (residence time). Since lakes and reservoirs are generally more quiescent than

Figure 9
Elevation vs River Mile

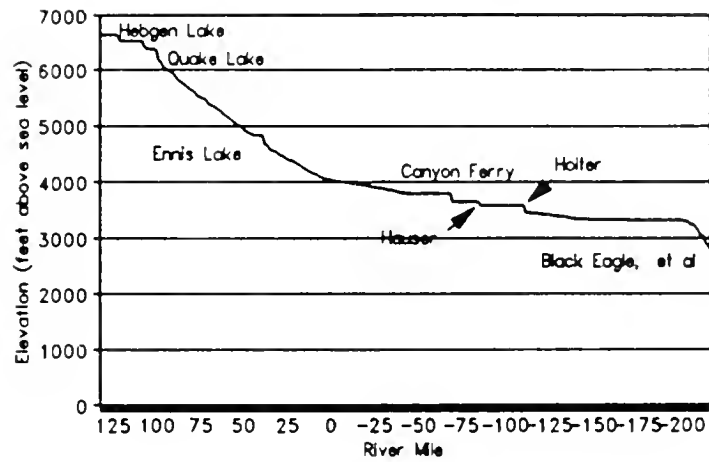


Figure 10
Drainage Area vs River Mile

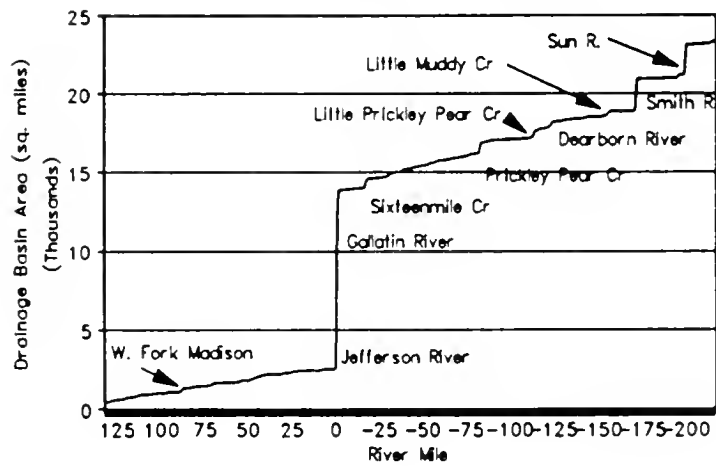


Table 4

Reservoir Data

Site	Capacity (ac. ft)	Capacity (cubic ft)	Average Flow (cfs)	Average Residence (days)	Source
Hebgen Lake	384840	1.676E+10	1004	193.25	1
Ennis Lake	42060	1.832E+09	1757	12.07	1
Toston Reservoir	3000	1.307E+08	5295	0.29	1,3
Canyon Ferry Lake	2050470	8.932E+10	5091	203.06	1
Hauser Lake	98230	4.279E+09	5096	9.72	1
Holter Lake	240420	1.047E+10	5545	21.86	1
Black Eagle Dam	1710	7.448E+07	7392	0.12	2
Rainbow Dam	930	4.052E+07	7742	0.06	2
Cochrane Dam	5873	2.558E+08	7742	0.38	2
Ryan Dam	2440	1.063E+08	7742	0.16	2
Morony Dam	7896	3.440E+08	7742	0.51	1,2

1. U.S. Geological Survey, 1991
2. Montana Power Company, 1992
3. Montana Department of Natural Resources, 1991

the run of the river, longer residence times allow greater proportions of suspended particles to settle out of the water column and into the sediments. Longer residence times also allow slower reactions (chemical, physical and biological) an opportunity to occur.

Table 5 estimates the travel time in the rivers, between reservoirs, based on river velocities calculated for several sites in the study area between April and September, 1991 (USGS, 1992, unpublished data). Table 6 uses the results from tables 4 and 5 to calculate the difference between the time an "average" water molecule would spend in rivers, and the time the same molecule would spend in reservoirs, as it travels through the study area. It shows that over 98% of the residence time in the study area is spent in reservoirs. This implies that if the components are available for sedimentation and coprecipitation in the system, there should be time for those processes to occur in the reservoirs based on the kinetics of arsenic (USEPA, 1987).

Where sedimentation is occurring the concentration of arsenic in the water column may decline as dissolved arsenic adsorbs onto particles, or crystallizes with other compounds, and falls into the sediments. Then, during a high water event, sediment may be scoured from the bottom and resuspended into the water column. When this occurs, higher mass quantities of total arsenic (dissolved plus suspended) will be found in the water column, even though

Table 5 Time of Travel Between Reservoirs

Hebgen Dam to Ennis Lake--Distance of 82 miles.

Mean Velocities recorded between 4/91 and 9/91:

<u>Site</u>	<u>Date</u>	<u>V(ft/sec)</u>	<u>V(mi/day)</u>
Below Hebgen Lake	4/11	2.57	42.1
	5/29	4.33	70.9
	7/15	2.80	45.8
	8/20	3.43	56.1
Kirby Ranch near Cameron	4/10	2.55	41.7
	5/29	5.10	83.5

Travel Time: Minimum = 23.6 hours Maximum = 47.2 hours
Average = 34.7 hours

Ennis Dam to Toston--Distance of 64 miles.

Mean Velocities recorded between 4/91 and 9/91:

<u>Site</u>	<u>Date</u>	<u>V(ft/sec)</u>	<u>V(mi/day)</u>
Below Ennis Lake	4/12	2.18	35.7
	5/28	4.15	67.9
	6/7	5.34	87.4
	7/15	2.71	44.3
	8/19	2.44	39.9
Toston	5/31	4.53	74.1
	6/7	6.25	102.3
	8/16	1.38	22.6
	8/23	1.55	25.4

Travel Time: Minimum = 15.0 hours Maximum = 68 hours
Average = 27.7 hours

Holter Dam to Black Eagle Dam--Distance of 93 miles.

Mean Velocities recorded between 4/91 and 9/91:

<u>Site</u>	<u>Date</u>	<u>V(ft/sec)</u>	<u>V(mi/day)</u>
Below Holter Dam	5/28	2.70	44.2
	6/12	4.89	80.0
	6/26	3.20	52.4
	8/15	2.42	39.6
Missouri River near Ulm	5/7	1.59	26.0
	6/14	2.54	41.6
	7/9	2.06	33.7
	8/26	1.85	30.3

Travel Time: Minimum = 27.9 hours Maximum = 85.8 hours
Average = 2 days, 3.3 hours

Source: USGS, 1992

Table 6Summary of Residence Times

<u>Reach</u>	<u>Mean Residence Time</u>
Hebgen Lake	193 days
Hebgen Lake to Ennis Lake	1.4 days
Ennis Lake	12 days
Ennis Lake to Canyon Ferry	1.2 days
Canyon Ferry, Hauser & Holter Lakes	235 days
Holter Lake to Black Eagle Dam (Great Falls)	2.1 days
Total for lakes	440 days (98.9%)
Total for rivers	4.7 days (1.1%)

the concentrations may be reduced by the diluting effect of the increased volume of water.

Study Area - Geology

The headwaters of the Madison River are in Yellowstone Park, where the surface is chiefly Quarternary and Tertiary volcanic rocks. These rhyolites are not likely to provide either the irons or clays necessary to partition arsenic to the sediments.

Outside Yellowstone Park, in the Madison River Valley, the river flows through Early Precambrian metamorphic rocks consisting of quartzofeldspathic gneiss, granulite, amphibolite, quartzite and marble. The river also encounters Tertiary basin fill, primarily as gravel, sand and silt. As in the headwaters, the products of these formations would not induce heavy sedimentation of arsenic. Some contact is made with the Madison limestone (Upper Paleozoic), shales from the Colorado Group (Cretaceous), and calcareous sandstone, shale and limestone of the Ellis Group (Lower Mesozoic); although the two latter formations have the capacity to provide clays to the Madison, they comprise only a relatively small percentage of the drainage.

The Madison River is fast-moving, as was demonstrated in Table 5. It would be unlikely to allow particles smaller than sands to settle, except in reservoirs.

Both the Gallatin and Jefferson rivers flow through similar geologic formations, if not the same formations. The Jefferson River, and its headwaters, encounter more of the Colorado Group and the Boulder Batholith (Cretaceous) than the Madison River encounters. The Gallatin River also drains a larger proportion of the Colorado Group.

The first large input of clays enters the Missouri River upstream of Toston. Here, Sixteenmile Creek brings weathering products of the Belt Supergroup, which is a Precambrian deposit containing argillites and shales. These mudstones would very likely introduce clays into the Missouri River.

From this point downstream in the study area, the surface geology is dominated by the Belt Supergroup, the Colorado Group, the Montana Group (Cretaceous shales, sandstones and siltstones) and the Kootenai Formation (Cretaceous conglomerate, sandstone, shale and mudstone). All of these formations would contribute clays to the Missouri River.

The geology section of the introduction is taken largely from Robert L. Taylor and Joseph M. Ashley's "Geological Map of Montana and Yellowstone National Park," Department of Earth Sciences, Montana State University, Bozeman, Montana 59717 (no date).

Literature Review

Stauffer, Jenne and Ball, 1980

Stauffer and Thompson, 1984

Stauffer et al. researched arsenic of geothermal origin in Yellowstone National Park, using the theory that geothermal waters represent a mixture of water from the high enthalpy magma dome, 2-3 kilometers below the surface, with meteoric water from the surface. Although the relative temperatures of springs and geysers can serve as an indicator of the relative percentages of hot (magmatic) water and cold (meteoric) water which comprise them, chemical constituents can be used as more accurate indicators. Chloride (Cl-) ions, for example, are highly conservative and abundant in geothermal waters. "Conservative," as applied by chemists, means that chloride, for example, does not react, precipitate or otherwise change its concentration once in solution. Because chloride concentrations are negligible in the meteoric water, the concentration of chloride in a mixed geothermal spring can be used as an indicator of the relative mixture of the two source waters.

Variation in the ratio of chloride to other components in the system may indicate whether the second component is of magmatic origin or leached from rock between the magma and the surface. Stauffer's data suggest the latter for arsenic.

Another explanation for changes in the ratio of chloride to another component can be that the second component is being removed from the system by reaction, precipitation, volatilization (off-gassing into the environment) or other process. Using this method of analysis Stauffer has found that total arsenic is conservative in the surface waters through Hebgen Lake.

Stauffer offers several explanations for arsenic's reluctance to precipitate here. First, the most effective scavengers of arsenic are hydrous iron oxides, which are found in very low concentrations relative to the arsenic in this system. In addition, where the springs are acidic, As(III) is the dominant arsenic species, and it is much less prone to adsorb onto hydrous iron oxides than is As(V). Where the springs are alkaline, As(V) is the dominant species, but adsorption is less likely to occur as alkalinity increases. In the acidic to neutral Gibbon River arsenic precipitates in quantity as As(III) is oxidized to As(V) along the reach before the acid is neutralized at the confluence with the alkaline Firehole River. But little of the As (V) is precipitated from the Firehole River, because of the high alkalinity and the relative scarcity of iron.

Finally, Stauffer found that precipitation of arsenic in Hebgen Lake was lower than might be expected because of short circuiting in the lake. Short circuiting often occurs

when a river entering a lake or reservoir is warmer than the reservoir by enough to cause the warmer (and less dense) river water to stay on top of the reservoir. Consequently, the two waters do not mix, and river water passes through the reservoir in much less than the average residence time without reacting with the sediments in the reservoir.

Sonderegger and Ohguchi, 1988

Sonderegger et al., 1982

Sonderegger and Sholes, 1989

The work of Sonderegger, Sholes, Ohguchi et al. examined the effects of irrigation in the lower Madison River valley. This valley has been irrigated with Madison River water for over 100 years. As a consequence the groundwater underlying the valley has become contaminated with high concentrations of arsenic, which flow back into the river through normal movement of the groundwater. The irrigation water evaporates at a relatively high rate, causing the arsenic to become more concentrated. The result is that the aquifer contains arsenic concentrations of as high as 150 ug/l adjacent to a section of the river where arsenic concentrations are in the range of 40-80 ug/l.

Other sources for the high concentrations of arsenic were sought in these studies, but extensive testing of the aquifer material revealed no other arsenic sources capable

of producing the observed concentrations (ibid.). Sampling of the river above the irrigation outflows and below the irrigation returns indicated increasing arsenic levels over this reach of the river, particularly during irrigation season and spring run off (when concentrations in the river are most dilute).

Knapton and Brosten, 1987

Knapton and Brosten, 1989

Knapton and Horpestad, 1987

Knapton, Horpestad and Brosten conducted three studies through the Madison and Missouri drainage between 1985 and 1988. Year-long data were collected on stream discharge, specific conductance, temperature, chloride and total recoverable arsenic at sites and tributaries from the headwaters in Yellowstone National Park to the Musselshell River at Mosby, Montana. From this data mass flux of arsenic was calculated.

Their data generally showed an increase in mass flux of arsenic during spring runoff, peaking at or before stream flow peaks, and a decrease in mass flux during falling stream flows in summer or early fall. This would coincide with the expected movement of sediments. Conversely, concentration of dissolved arsenic varied inversely with stream flow, approximately, as a result of dilution during high water.

U.S. Geological Survey, 1977-1992

The U.S. Geological Survey maintains records of stream flows and water quality throughout the United States. As a result, stream flow data are available for all of the Missouri River sites in this study and at or near most of the other sites. In addition, extensive water quality data is available for the Toston site for over twenty years and intermittently for West Yellowstone and other sites. This has provided a long term context for this short term study, and U.S.G.S. data have been used in the procedure and experimental results sections which follow.

Mok, 1988Mok and Chien, 1990

Mok has conducted several studies of creeks and rivers which have been impacted by mining activity in Idaho. Mining has stopped at both the Blackbird Mine, which drains into the Salmon River by way of Blackbird Creek, and at Kellogg, Idaho, which drains into Lake Coeur d'Alene by way of the South Fork and the main stem of the Coeur d'Alene River. In both cases tailings and dumps at the mines are rich in iron pyrite (FeS_2) and arsenopyrite (FeAsS). Through the processes of oxidation and leaching the drainage from these sites becomes acidic and enriched in both iron and arsenic (among other metals).

At the Blackbird site, As(V) is the dominant species throughout the drainage. In the upper portions of the drainage, closest to the mine site, the water is mildly acidic, and the sediments are very high in both arsenic and iron. As the pH rises downstream (by dilution from other sources) there is a corresponding increase in the release of arsenic from the sediments. Leaching experiments verified that arsenic becomes adsorbed to iron oxides and coprecipitated with hydrous iron oxides at neutral to mildly acidic pH, but that arsenic is released at more acid (pH <3.5) and more alkaline (pH >8) conditions. This is contrary to the behavior of most metals, which are released at increasing rates with decreasing pH.

In the Coeur d'Alene River As(III) dominates over As(V) from the mine site downstream to Coeur d'Alene Lake. Mok attributed this to the removal of As(V) by adsorption and coprecipitation with iron species, and the slow oxidation rate of As(III) in the river. As(V) is much prone to these partitioning processes than As(III) at the average pH of 7.5 found in the South Fork and the main stem of the river. Here again, leaching experiments related the release of arsenic from the sediments to pH.

One of the treatments used to stop the release of metals from acid waters is the addition of lime to raise the pH. Mok noted that this practice may cause the release of arsenic if the pH is raised above the neutral level.

Moore, Ficklin and Johns, 1988

Moore, Ficklin and Johns have studied the Clark Fork River near Missoula, Montana. This is the farthest downstream section of the river included in the largest EPA Superfund site, the Clark Fork Complex. Contamination of this site originated with the copper mining operations at Butte, Montana, and copper smelting operations at Anaconda, Montana, 100-120 miles upstream. Sediments behind the Milltown Dam near Missoula have accumulated massive amounts of arsenic, iron, copper, cadmium, lead and other metals.

Segments of core samples were analyzed for pH, dissolved oxygen, oxidation potential (Eh), ferrous (reduced) iron, sulfide, As(III), As(V) and organic arsenic. The core sample was 115 cm in depth. The pH declined from 8.0, at the sediment surface, to 7.0 from 80 centimeters below the sediment surface to the bottom of the core, at 115 centimeters. Dissolved oxygen peaked at less than 2 ppm at 30 cm, then dropped to zero at 75 cm and remained at zero from there down. Ferrous iron was below detection to 45 cm, then increased relatively steadily; total iron (ferrous plus ferric) remained relatively constant throughout the column. Organic arsenic, and the ratio of As(V) to As(III), increased to 15 cm, then decreased steadily. The water found in the spaces between the sediment particles (interstitial water) contained little or no dissolved arsenic above the reducing zone, but high concentrations were found within the

reducing environment. Sulfide behavior was similar to that of ferrous iron.

The authors explain that biological activity in the upper 70-80 cm of the sediments consumes all of the available oxygen, creating a reducing environment. This, in turn, reduces sulfate (SO_4^{2-}) to sulfide (S^{2-}), and ferric iron $[\text{Fe(III)}]$ to ferrous iron $[\text{Fe(II)}]$. When ferric oxyhydroxides are reduced to ferrous oxyhydroxides, they become significantly more soluble, releasing the arsenic and other metals which had coprecipitated with them or were adsorbed onto them. Insoluble (in a reducing environment) iron and metal sulfides are formed, reversing the processes which oxidized and dissolved iron pyrites upstream, and pH should rise. But some metals and arsenic are released into the interstitial water and, travel from there into either the water column or the ground water.

The conditions studied by these researchers do not always match those in the Madison and Missouri Rivers. Nevertheless, the same processes may be occurring to a greater or lesser degree in the study area.

Experimental Procedure

Sampling Sites

The sampling sites are shown in figures 5 and 6 (pages 20 and 21. Additional information about the sites is as follows:

A. Ennis (Madison County, T6S, R1W, Section 4, tract ADC), on the Madison River. The sampling site was the farthest upstream site in the fishing access across the Madison River from the town of Ennis. The river bottom ranged from boulders to coarse gravel, but was primarily cobbles. The nearest USGS gaging station (#06041000) is the dam below Ennis Lake, eleven miles downstream.

B. Black's Ford (Gallatin County, T25S, R2E, Section 19, tract DBA), on the Madison River. The sampling site was the first turnaround on the unnumbered gravel road between state highway 84 and Trident, Montana. The river bottom ranged from boulders to coarse gravel, but was primarily cobbles. The nearest USGS gaging station (#06041000) is the dam below Ennis Lake, 15 miles upstream.

C. Madison River at U.S. Highway 10 (Gallatin County, T2N, R2E, Section 30, tract BAB). The sampling site was 1/4 mile north on the dirt road just west of the bridge over the Madison River on U.S. Highway 10. The river bottom ranged from boulders to coarse gravel, but was primarily cobbles.

The nearest USGS gaging station (#06041000) for the Madison River is the dam below Ennis Lake, 38 miles upstream.

D. Jefferson River (Broadwater County, T2N, R1E, Section 27, tract BCD). The sampling site was on the south west side of the U.S. Highway 10 bridge across the Jefferson River, on the west side of the river. The river bottom ranged from boulders to sand, with various areas dominated by sand, or gravel or cobbles. The site is about two hundred yards upstream of a USGS gaging station (06036650).

E. Toston (Broadwater County, T5N, R2E, Section 23, tract CAA) on the Missouri River. The sampling site was on the east side of the Missouri River on the north side of the bridge between U.S. Highway 287 and Toston, Montana. The river bottom ranged from cobbles to silts, but rocks below the surface made it difficult to push a probe into the mud bottom more than a foot. The site is 2.4 miles downstream from a USGS gaging station (#06054500).

F. Canyon Ferry Dam (Lewis and Clark County, T10N, R1W, Section 4, tract DDB) on the Missouri River. The sampling site was on the north east side of the river, below the powerplant. The river bottom ranged from boulders to sand. The powerplant is a gaging station (#06058500).

G. Sun River (Cascade County, T20N, R3E, Section 15, tract AAC). The sampling site was on the south side of the Sun River, west of the 6th Street NW bridge in Great Falls.

The river bottom was fine sand and silt. The nearest USGS gaging station on the Sun River (#06089000) is 13 miles upstream at Vaughn, Montana.

H. Missouri River at Ulm, Montana (Cascade County, T19N, R3E, Section 5, tract BBA). The sampling site was twenty yards upstream of the USGS gaging station (#06078200). The river bottom was fine sand and silt.

J. Morony Dam (Cascade County, T21N, R5E, Section 11, tract CDC) on the Missouri River. The sampling site was on the west side of the river, about 150 yards below the dam and 80 yards upstream from the USGS gaging station (#06090300). The river bottom ranged from boulders to sand.

Sampling Procedure

For each sample, field values of pH, water temperature, conductivity and alkalinity were determined as described below. Each sample was collected through a peristaltic pump.

The inlet for the tubing was placed in a moving current, as close as possible to the main channel. The open end of the tubing was secured by tape to a 136 centimeter steel pipe with the opening 46 cm from the bottom. In this way, if the pipe was placed at an angle such that the top was even with the surface, then the inlet was about one-third the distance from the bottom to the surface. This is

the depth at which the stream velocity approximates average velocity in vertical section at the sampling point. At sites where the pipe was secured by setting it into mud (rather than resting it on rocks) measurements were performed to ascertain the appropriate depth for the inlet, which was then repositioned to that depth.

Next, the probe for a YSI Model 3000 T-L-C Meter (temperature-level-conductivity) was placed near the inlet tube on the stream bed. The meter housing was secured to the bank. A back-up conductivity meter of the same brand and model was used to cross-check this meter at least once on each trip. The two conductivity meters never varied by more than 2 micromhos/cm or 0.2 ° C.

An Orion Research model SA 230 meter was used to read pH and temperature at the surface. An Orion combination pH probe 91-06 was used along with an ATC (automatic temperature compensation) probe. The meter was calibrated against standard buffer solutions at the first site each day, using pH 7.0 and pH 10.0 buffers and the ATC two buffer method. A second pH meter of the same brand and model, varied by no more than 0.10 pH units and 0.2 °C from the first meter.

After the YSI meter had equilibrated with the stream, temperature and conductivity readings were recorded. Specific conductance was read on the 2 millimhos/cm scale, temperature compensated to 25 °C by the meter.

The final on-site reading was alkalinity. A 100 ml sample was taken from the stream near the tubing inlet using a 100 ml graduated cylinder. This sample was transferred to a 250 ml cup with a top wide enough to allow both the temperature and pH probes from the Orion meter to be used for both endpoint determination and stirring of the sample/acid solution. A Hach Digital Titrator was used to deliver measured increments of acid to the sample. A Hach Digital Titration Cartridge of sulfuric acid $1.600 \pm 0.005\text{N}$ was employed in the titrator unit. This gave a direct readout in mg/l of CO_3^{2-} plus HCO_3^- as CaCO_3 .

Some difficulty was encountered with broken "hooks" (long, plastic tubes used to deliver fine quantities of acid to the solution) and leaking from the point where the hook was inserted into the cartridge. When these problems occurred the hooks and acid cartridges were replaced, and fresh samples were analyzed.

Tubing from the inlet was attached to one of the two peristaltic pumps. The time required to prime the pump at high setting was noted, and the pump was allowed to run for at least three of these time periods before any samples were taken; this procedure was to minimize possible contamination from previous sites. Sample bottles were labelled with the site (letter code), sample run number, whether the sample was filtered or raw (unfiltered), and whether the sample was acidified (preserved) or unacidified.

Raw acidified samples were taken in one liter bottles and preserved with five ml of nitric acid (HNO_3) pre-measured into glass ampules. These were used to determine the total recoverable arsenic.

Filtered samples were filtered through 0.45 micrometer pore size cellulose acetate filters. The filters were 102 mm in diameter and held in a plexiglass filter holder between two coarse filter screens. Geotech Environmental Equipment, Inc., brand Geofilters were used. One filtered sample was acidified for use in determining arsenic redox state [concentration of arsenic(III), and concentration of arsenic(V)]. A second filtered sample was left unacidified for use in determining total dissolved arsenic.

The filtered acidified samples of the first three sample runs were preserved with nitric acid rather than hydrochloric acid (HCl). Accepted theory is that nitric acid oxidizes As(III) to As(V), invalidating the redox analyses. In the fourth sample run duplicate filtered acidified samples were prepared at three sites. One duplicate was preserved with nitric acid and the other with hydrochloric acid. The samples preserved with nitric acid showed redox results identical to the samples preserved with hydrochloric acid in two samples, and a higher percentage of As(III) in the third sample. For this reason the redox data in the first three sample runs were considered valid in the study.

Filtered acidified samples were taken in 250 ml sample bottles. Those preserved with nitric acid were treated with 1.5 ml HNO_3 from pre-measured glass ampules. Filtered acidified samples preserved with hydrochloric acid were treated with 1.75 ml HCl using a two ml pipette and bulb.

Suspended sediment samples were collected using an in-line filter holder on the same pumps used for the water sample collection. The filter holder sandwiched the filters between coarse mesh filters. Geotech 0.45 micrometer cellulose acetate filters, 102 mm in diameter, were used. Each filter was used until it became so clogged that, either the silicon tubing began to swell or the filtrate leaving the filter was reduced from a stream to drops. To ensure that enough sediment had been obtained to exceed the lab's detection limits, two to four filters were collected for each sample, the great majority consisting of three filters. The sediment laden filters were folded and stored in centrifuge tubes, one tube per sample.

Filtrate from the sediment samples was collected and measured using a one liter graduated cylinder. This, plus the volume of the filtered samples, constituted the total volume of water from which the sediment sample was obtained. Combined with the mass of arsenic in the sediment sample, as reported by the lab, this provided the concentration of suspended arsenic in the sample.

Both the sediment and the filters were digested and analyzed for arsenic content by the lab. For this reason a "sample" of six filter blanks (twice the number used in the majority of samples) was run by the laboratory to determine background levels of arsenic in the filters. The lab reported an arsenic content of 0.1 ug for the six filters combined.

The exception to the above procedure for sediment sample collection was a single sample collected at the Toston site. Here the sediment was separated into a coarse fraction and a fine fraction. The sample was first pumped through a 200 mesh (65 micrometer) screen and collected in an acid washed gerry can. This coarse sample was then rinsed into a sample collection bag using deionized water. The coarse filtered water was then re-pumped through the 0.45 um filters as above, being careful to keep the sediment in the sample suspended through agitation throughout the sample. In order to obtain enough coarse sediment for a viable sample a much larger volume of stream water needed to be sampled than in any of the other samples. Forty-one liters of river water were run through the coarse screen; due to leakage problems with the filter holder only about thirty-seven liters passed through the fine fraction filters. This required eighteen of the cellulose acetate filters (three of which were 152 mm filters in a new, leaky, filter holder).

At sampling sites which were within about fifty meters of the car a Geotech Environmental Equipment Geopump 2 peristaltic pump was used. It was powered by a 12-volt recreational vehicle battery and remained in the vehicle.

At sites which were farther from the car than could be reached with tubing, a Horizon Ecology Company Portable Masterflex Sampling Pump, model 7570-10, was used. Powered by its internal, sealed lead-acid battery, the Masterflex was portable, but less powerful and, therefore, slower.

Laboratory Analysis

All laboratory analyses were performed by the chemistry laboratory of the Montana Department of Health and Environmental Sciences. The following instruments were used:

Perkin-Elmer ICP/5500 Inductively Coupled Plasma with

P-E Atomic Spectroscopy Data System 10

Perkin-Elmer 5100 Atomic Absorption Spectrophotometer

with

-Zeeman 5100 Furnace Module

-HGA 600 furnace, programmer and supply

-As 60/70 autosampler

-7700 Professional Computer system.

Analyses for total recoverable and total dissolved arsenic were performed using method 206.2 from Standard Methods for the Examination of Water and Wastewater, 16th Edition.

Method 15.0, from the same source, was used for redox

analysis. Sediment arsenic was analyzed using the method from Methods for Chemical Analysis of Water and Wastes, Environmental Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, March 1979. (Halm, 1992)

Quality Assurance

For both total recoverable and total dissolved arsenic the lab's detection limit was 0.001 mg/l (1 ug/l), with an accuracy of +/- 0.002 mg/l. The same applied to the redox sample concentrations, but, because each sample was diluted 3:1, the effective detection limit was 0.004 mg/l, with an accuracy of +/- 0.008 mg/l. The detection limit on the sediment samples is 2.5 micrograms As per sample for the first five sample runs, and 0.1 micrograms As per sample on subsequent runs with a different ICP in use.

In addition to the lab's internal quality assurance program one blind duplicate sample was submitted, and one series of three replications was submitted. For the blind duplicate sample the precision was as follows:

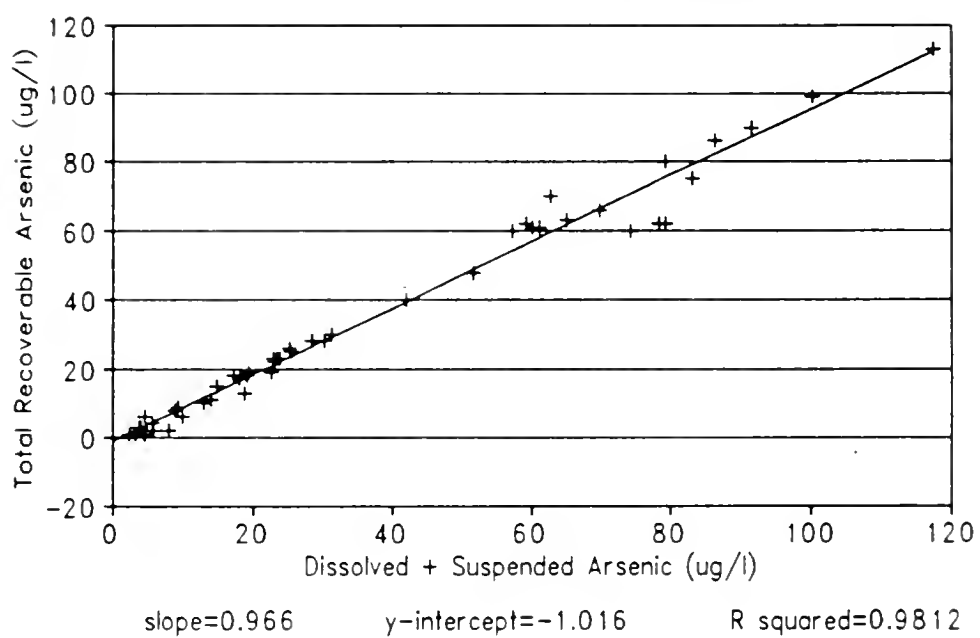
	variation	% variation
Total recoverable As	+/- 1 ug/l	1.64
Total dissolved As	+/- 1 ug/l	1.72
As(V)	+/- 6 ug/l	11.1
Suspended As	+/- 0.01 ug/l	2.94
As(III)	all samples at or below detection.	

For the replicate samples the precision was as follows:

	variation	% variation
Total recoverable As	+/- 0.94 ug/l	1.5
Total dissolved As	+/- 2.2 ug/l	2.8
As(V)	+/- 0.94 ug/l	1.5
Suspended As	+/- 0.022 ug/l	6.2
As(III) two samples at < detection, one at 8 ug/l.		

It was noted that total recoverable arsenic was occasionally reported to be lower than total dissolved arsenic, both in this study and in USGS data. This is a theoretical impossibility. Mok proposed that suspended sediment has a tendency to adhere to the walls of sample bottles, and adsorb additional dissolved As, causing the sample concentrations to be understated (Mok, 1988). Because both dissolved and suspended arsenic had been determined separately for the study, it was suggested that the sum of these two tests be used in place of the single test results for total recoverable arsenic. Figure 11 plots the reported total recoverable arsenic against the sum of the reported dissolved and suspended arsenic. If the two methods of determining total recoverable arsenic gave identical results the slope of the line and the correlation coefficient would each equal one, and the y-intercept would be zero. The plot shows a very good correlation between the two with dissolved-plus-particulate arsenic being about five per cent higher on average than the reported total arsenic. For the

Figure 11
Total As vs. Dissolved + Suspended As



purpose of this study, the ratio of dissolved-As-to-suspended-As and consistency are more significant than the precise numbers.

Finally, because USGS data are available for three sites from West Yellowstone to Toston for the same water year, Tables 7 and 8 show the USGS data along with the data from this study for comparison. The two data sets are in close agreement.

Table 7 - USGS Data vs. This Study, Madison Sites

Sample	Date	Spec Cond (us/ cm @ 25C)	Alka- linity (mg/l as CaCO3)	Total Recov- erable Arsenic (ug/l)	Total Dis- solved Arsenic (ug/l)	Flow (cfs)	Site
USGS	10/23	514		240		406	Madison
USGS	02/12	559		280		377	River
USGS	04/11	550		340		422	near W.
USGS	05/29	268		120		1060	Yellow-
USGS	06/19	364		170		604	stone
USGS	07/16	448		260		429	
USGS	08/21	460		270		391	
A-1	05/09	331	103	113	116	1090	Ennis
A-2	05/23	290	99	99	95	1610	Ennis
A-3	06/06	221	84	60		6680	Ennis
A-4	06/17	219	75	61	59	2510	Ennis
A-5	06/24	220	75	63	64	2630	Ennis
A-6	08/29	268	92	86	86	1560	Ennis
A-7	09/10	268	91	90	94	1870	Ennis
USGS	10/24	305		54		1920	Below
USGS	02/11	348		57		1320	Ennis
USGS	04/12	321		63		1060	Lake
USGS	05/28	306		81		3640	
USGS	06/19	236		35		2870	
USGS	07/15	259		70		1490	
USGS	08/19	278		88		1140	
B-2	05/23	124	69	19	18	1610	Black's
B-3	06/06	176	68	38		6680	Ford
B-4	06/17	177	65	40	41	2510	
B-5	06/24	189	69	48	50	2630	
B-6	08/29	274	107	80	79	1560	
B-7	09/10	278	104	66	62	1870	
C-1	05/09	328	114	75	75	1090	Madison
C-2	05/23	267	125	70	59	1610	@ Hwy 10
C-3	06/07	231	82	62		6680	
C-4	06/18	226	83	61	59	2510	
C-5	06/24	230	88	66	69	2630	
C-6	08/29	290	109	90	91	1560	
C-7	09/10	283	105	74	82	1870	
C-8	09/19	287	109	60	74	1630	
C-9	09/19	287	111	62	79	1630	
C-10	09/19	286	102	62	78	1630	

Table 8 - USGS Data vs. This Study

Missouri River Sites							
Sample	Date	Spec Cond (uS/ cm @ 25 C)	Alka- linity (mg/l as CaCO3)	Total Recov- erable Arsenic (ug/l)	Total Dis- solved Arsenic (ug/l)	Flow (cfs)	Site
E-1	05/10	341	132	23	21	4140	Toston
E-2	05/23	221	104	15	11	11300	Toston
E-3	06/07	207	79	21		21500	Toston
E-4	06/18	225	86	18	17	9740	Toston
					16		
E-5	06/25	240	98	23	23	7870	Toston
E-6	08/30	341	139	62	59	1510	Toston
EA-6	08/30	341	139	60	57	1510	Toston
USGS	11/28	378	139	42	43	3590	Toston
USGS	03/07	400	146	32	27	2780	Toston
USGS	06/12	213	79	17	19	18800	Toston
USGS	08/20	342	120	54	50	1120	Toston
USGS	09/02	345	125	69	67	1490	Toston
N-7	09/10	286	100	72	75	1870	Ennis
Q-7	09/10	279	98	70	75	1870	Grey- cliff
R-7	09/10	281	101	72	76	1870	Cobble- stone

Experimental Results

This study was designed to research the mobility and transport of arsenic in the study area. The results will be discussed, followed by a comment on the data from the Black's Ford site. Complete raw data from the study is in, Appendix B.

Conservatism

In the strictest sense arsenic is, by its elemental nature, conservative. But as discussed in the literature review, a headwater source of arsenic can be moved from the water column into the sediments through physical or chemical reactions. There it may become a source of arsenic when the concentration gradient becomes reversed, desorption occurs, or the sediments are re-entrained during a scouring event.

If arsenic is traveling through the system without accumulating in sediments or changing forms, then the element's behavior is conservative. Unfortunately, in a system of river runs interspersed with reservoirs of various sizes, conservatism is not easy to demonstrate.

A concentration peak in the river may be moderated in a reservoir, by mixing with water of lower concentration (dilution) and/or by delay (residence time) in the reservoir. If the reservoir exhibits strong seasonal variations in mixing and flow regimes, as a result of stratification, for example, years of continuous sampling above and below a

reservoir may be necessary to determine if everything which enters the reservoir exits as well.

Conservatism may be determined by mass flux, which is the mass quantity of the substance which passes by a given reference point during a given period of time. It is commonly stated in terms of pounds per day. Mass flux is determined by multiplying concentration (mass of solute per unit volume of solution), times discharge of solution (volume per unit time), times a correction factor for units (in this case to correct micrograms/liter times cubic feet/second to lbs/day).

$$M = C * Q * 5.39$$

This provides only an approximation because of the many assumptions and errors inherent in the two factors. For example, it must be assumed that concentrations and discharges are constant with respect to time, and that they accurately measured in both the field and the lab. Because sampling sites were as far as 38 miles from the gaging stations used in determining their discharges, inaccuracies are likely in discharge values.

Figure 12 summarizes mass flux of arsenic on a site by site basis during this study. Each bar represents one of the six samples taken at that site. The range of values at sites above Canyon Ferry was reduced by the reservoir. Mass flux at Ennis and at Highway 10 follow a very similar pattern despite having Ennis Lake between them; this is because

Figure 12
Mass Flux Arsenic by Site by Sample

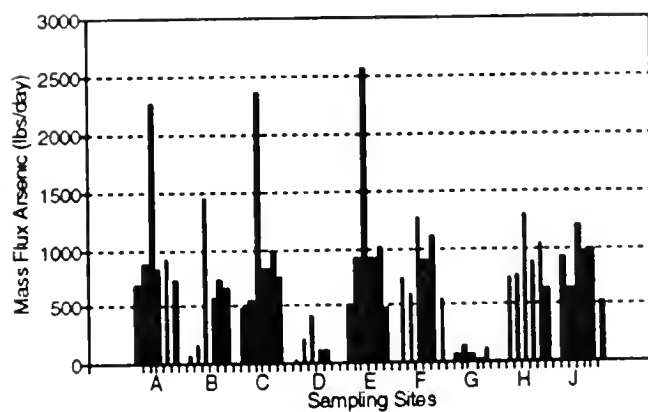
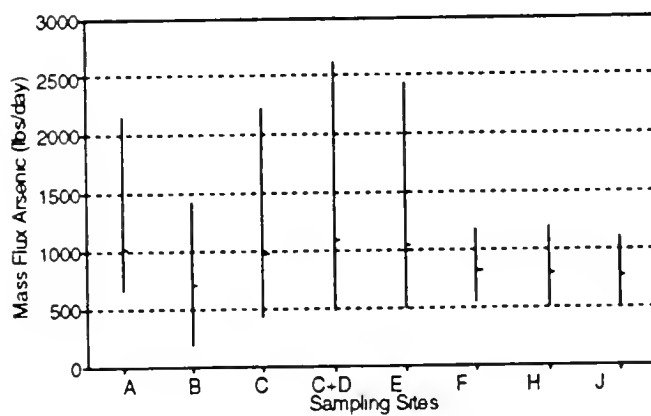


Figure 13
Mass Flux Range & Mean, by Site



A. Ennis B. Black's Ford C. Madison at Highway 10
D. Jefferson E. Toston F. Canyon Ferry G. Sun River
H. Missouri River at Ulm J. Morony Dam

of the relatively short average residence time for that reservoir (twelve days). The higher values at Toston can be attributed to the addition of arsenic from the Jefferson River, as shown in Table 9.

It is difficult to correlate mass flux above and below a reservoir which has as substantial an average residence time (203 days) as Canyon Ferry. Figure 13 attempts to approach that goal, by averaging mass flux for the six samples from each site shown in Figure 12. High and low values for each site are indicated by the top and bottom of the vertical line, respectively, and the mean is indicated by the dash through the vertical line.

Two features of Figure 13 are the drop in the mean between Toston and Canyon Ferry, and the low value at Black's Ford. Because the average residence time at Canyon Ferry Reservoir is about seven months, and this study was conducted over less than four months, it is impossible to determine if the average residence time alone accounts for this drop. Neither feature is statistically significant above a 90% confidence level.

Table 9 shows the loss or gain of arsenic between sites, and the overall loss or gain for the study area. Thirteen of the thirty-one changes fall within ten percent, and only eight are greater than twenty percent. When the averaged figures are used (as in Figure 13) only Canyon Ferry showed a change of more than seven percent; as noted

Table 9 - Changes in Mass Flux by Percent by Site

Date*	Ennis (lbs/ day)	Madison, Hwy 10 (lbs/day)	% Change	Madison, Hwy 10 + Jefferson (lbs/day)	Toston (lbs/day)	% Change
05/09	664	441	-33.6	466	513	10.1
05/23	859	607	-29.3	795	914	15.0
06/07	2160	2232	3.3	2622	2434	-7.2
06/17	825	825	0.0	968	945	-2.4
06/24	893	935	4.7	1009	976	-3.3
08/29	723	757	4.7	760	497	-34.7
09/10	907	746	-17.8			

Average	1004	935	-6.9	1103	1046	-5.2

Date*	Toston (lbs/ day)	Canyon Ferry (lbs/day)	% Change	Canyon Ferry (lbs/day)	Missouri, at Ulm (lbs/day)	% Change
05/10	513	699	36.3	699	500	-28.5
05/23	914	614	-32.8	614	713	16.1
06/07	2434	1192	-51.0	1192	1207	1.3
06/18	945	880	-6.9	880	828	-5.9
06/25	976	1010	3.5	1010	873	-13.6
08/30	496.5	539	8.6	539	627	16.3

Average	1046	822	-21.4	822	791	-3.8

Missouri, at Ulm, + Sun				<u>Summary</u> Full Study Area		
Date*	(lbs/day)	Morony Dam (lbs/day)	% Change	Ennis (lbs/day)	Morony Dam (lbs/day)	% Change
05/15	514	701	36.4			
05/28	760	601	-18.3			
06/10	1264	1125	-11.0			
06/20	838	905	8.0	664	701	5.6
06/26	898	777	-13.5	859	621	-27.7
08/31	630	534	-15.2	2160	1125	-47.9

Average	817	777	-4.9	825	905	9.7
				893	777	-13.0
				723	534	-26.1

				1021	777	-23.9

*Dates are for the first column, and within five days otherwise.

above, the average residence time for Canyon Ferry exceeds the sampling period by a large enough amount to preclude drawing any firm conclusions from this data.

If the only process affecting the arsenic is dilution, then it is behaving conservatively. This can be determined by analysis of arsenic concentrations in the study area.

Figures 14 and 15 are prepared in the same way as figures 12 and 13, except that they use arsenic concentrations instead of mass flux. Again the moderating effect of Canyon Ferry is evident. The reduced concentrations from Highway 10 to Toston demonstrate the diluting effect of the Gallatin and Jefferson rivers (Figure 15).

Because data are available for all four rivers, the mixing of the Madison, Jefferson and Gallatin rivers to form the Missouri River provides a useful example of mixing and its effect on concentration. Table 10 compares the total arsenic concentration measured at the Toston site with the concentration calculated by combining the three headwater streams mathematically. The sum of the discharges for the three headwater rivers was combined with the sum of the mass flux calculated from their reported arsenic concentrations to arrive at a predicted concentration at their confluence (represented by Toston). Because arsenic data were only available for the first sample on the Gallatin River, and it constituted less than three percent of the arsenic in the

Figure 14
Arsenic Concentration by Site by Sample

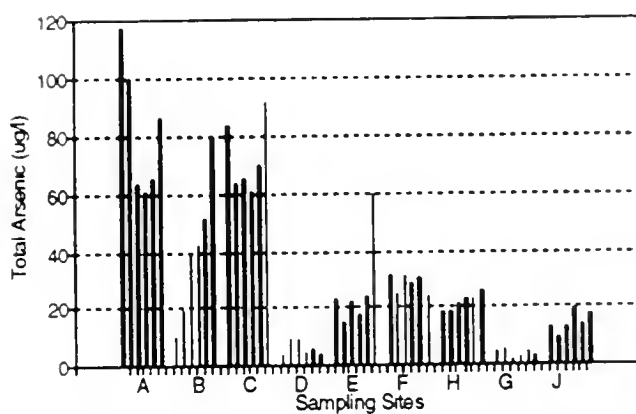
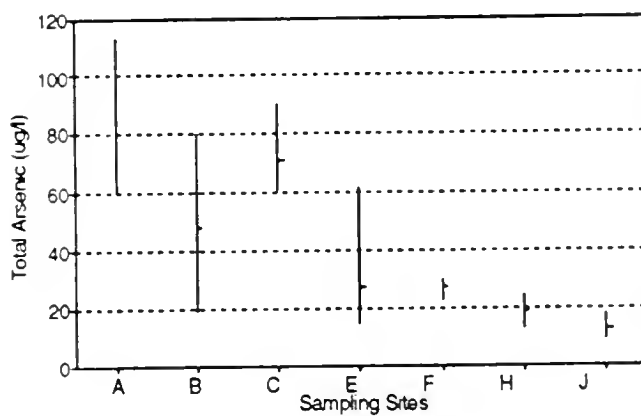


Figure 15
As Concentration Range & Mean, by Site



A.Ennis B.Black's Ford C.Madison at Highway 10 D.Jefferson
E.Toston F.Canyon Ferry G.Sun River H.Missouri River at
Ulm J.Morony Dam

Table 10 Concentration Mixing,
Missouri River Headwaters

Date	Madison @ Hwy 10		Jefferson River		Gallatin River *	
	Total As (ug/l)	Stream Discharge (cfs)	Total As (ug/l)	Stream Discharge (cfs)	Total As (ug/l)	Stream Discharge (cfs)
05/09	75	1090	3	1570	2	1190
05/23	70	1610	8	4350	2	4720
06/07	62	6680	9	8040	2	6910
06/18	61	2510	6	4410	2	3000
06/24	66	2630	4	3410	2	2400
08/29	90	1560	3	180	2	345

* All arsenic concentrations for the Gallatin River are based on the 5/09/91 sample; stream discharges as per USGS.

Combined Gallatin, Missouri River Madison & Jefferson at Toston						
Date	Total As (ug/l)	Stream Discharge (cfs)	Total As (ug/l)	Stream Discharge (cfs)	Percent Change, Conc.	Percent Change, Discharge
05/09	23	3850	23	4140	-0.3	7.5
05/23	15	10680	15	11300	2.1	5.8
06/07	23	21630	21	21500	-9.2	-0.6
06/18	19	9920	18	9740	-3.8	-1.8
06/24	23	8440	23	7870	1.1	-6.8
08/29	68	2085	61	1510	-10.2	-27.6

three headwater rivers combined, that concentration was assumed to be constant for the sampling period. The percentage change in concentration and stream discharge, shown in the last columns of the bottom half of the table, are all within ten percent, except for the last sample run. With the low stream flows for the Jefferson and the Gallatin, which are the result of irrigation withdrawals, and a further drop in stream discharge between the gaging stations on the headwater streams and Toston, the concentration reduction of 10.2 percent may be accounted for by taking a larger percentage of the discharge drop from the high arsenic concentration Madison River, and a lower proportion from the diluting concentrations in the two other headwater streams.

Using a constant input modeling technique, an appropriate, theoretical mass per day of arsenic can be mathematically applied to the headwaters of the Madison. This mass per day is divided by the stream discharge at each sampling site, resulting in a theoretical concentration. If these theoretical concentrations are graphed against the measured concentrations, and they are a perfect match, then the line they create will have both a slope and a correlation coefficient of one (1.0).

Table 11 compares a theoretical concentration for each sample with the measured concentration. Using trial and error it was found that a mass of arsenic of 731.5 lbs/day of arsenic yielded a slope of 0.99992 and an R^2 value of 69

Table 11 - Concentration: Experimental vs. Theoretical

for mass As = 731.5 lbs/day

Site	Date	Flow (cfs)	Theoretical Arsenic (ug/l)	Measured Arsenic (ug/l)
Ennis	05/09	1090	125	113
Madison, Hwy 10	05/09	1090	125	75
Toston	05/10	4140	33	23
Canyon Ferry	05/14	4320	31	30
Ulm	05/15	7130	19	13
Morony Dam	05/15	13000	10	10
Ennis	05/23	1610	84	99
Black's Ford	05/23	1610	84	19
Madison, Hwy 10	05/23	1610	84	70
Toston	05/23	11300	12	15
Canyon Ferry	05/24	4380	31	26
Ulm	05/28	7780	17	17
Morony Dam	05/28	12800	11	9
Ennis	06/06	6680	20	60
Black's Ford	06/06	6680	20	38
Madison, Hwy 10	06/07	6680	20	62
Toston	06/07	21500	6	21
Canyon Ferry	06/07	7370	18	30
Ulm	06/10	11200	12	20
Morony Dam	06/10	17400	8	12
Ennis	06/17	2510	54	61
Black's Ford	06/17	2510	54	40
Madison, Hwy 10	06/18	2510	54	61
Toston	06/18	9740	14	18
Canyon Ferry	06/18	5830	23	28
Ulm	06/20	6980	19	22
Morony Dam	06/20	9330	15	18
Ennis	06/24	2630	52	63
Black's Ford	06/24	2630	52	48
Madison, Hwy 10	06/24	2630	52	66
Toston	06/25	7870	17	23
Canyon Ferry	06/25	6690	20	28
Ulm	06/26	8520	16	19
Morony Dam	06/26	13100	10	11
Ennis	08/29	1560	87	86
Black's Ford	08/29	1560	87	80
Madison, Hwy 10	08/29	1560	87	90
Toston	08/30	1510	90	62
Canyon Ferry	08/30	4350	31	23
Ulm	08/31	4650	29	25
Morony Dam	08/31	5500	25	18

percent. Figure 16 plots the theoretical concentration against the measured concentration.

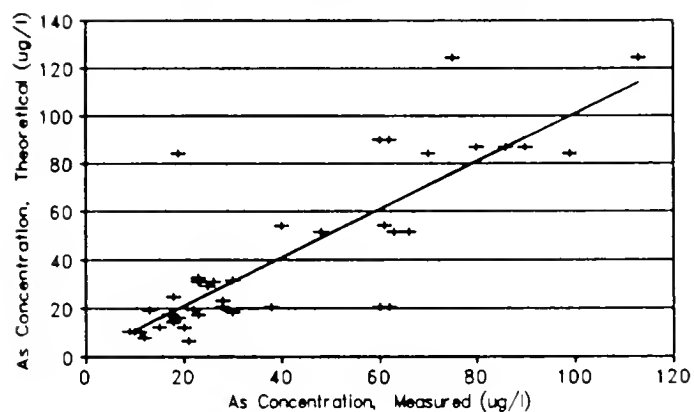
The USGS data for West Yellowstone (Table 7) have a mean mass loading rate of 611 lbs/day of arsenic; the values ranged from 525 lbs/day on 10/23/90 to 773 lbs/day on 4/11/91. Using data from this study (Table 9) for the Ennis site, the mean mass loading was 1004 lbs/day; the values ranged from 664 lbs/day on 5/9/91 to 2160 lbs/day on 6/7/91. If these fluctuations accurately reflect fluctuations in the arsenic source, then an R^2 value of 69 percent over the same time period may not be unreasonable for a conservative system (Figure 16).

Figure 17 is identical to Figure 16, except that the mass loading applied to each sample run was the mass loading calculated for the Ennis site for that run. This allowed the mass loading to vary with the source. The plot has a slope of 0.996 and an improved R^2 value of 75.8 percent. Although the results of figures 16 and 17 show a good correlation between concentration and dilution in the study area, they are not convincing evidence that only dilution is affecting the arsenic concentration.

Partitioning

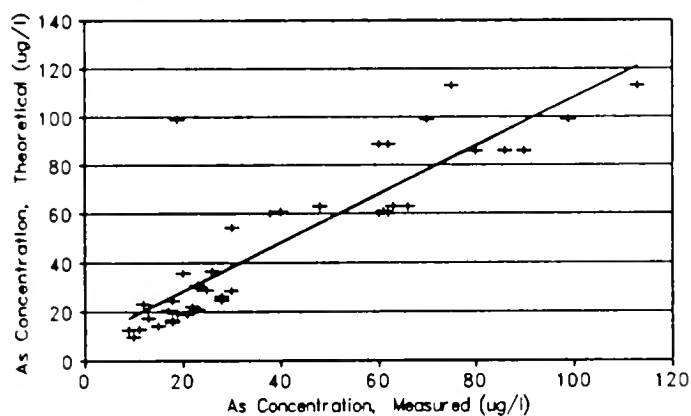
To clarify the results of the partitioning of arsenic between the dissolved and particulate phases in this study, the particulate phase arsenic concentration has been divided

Figure 16
Concentration, Theoretical vs Measured



for M=731.5 lbs/day As $Y=0.99992X+0.909$ $R^2=0.691$

Figure 17
Conc., Theoretical vs Measured



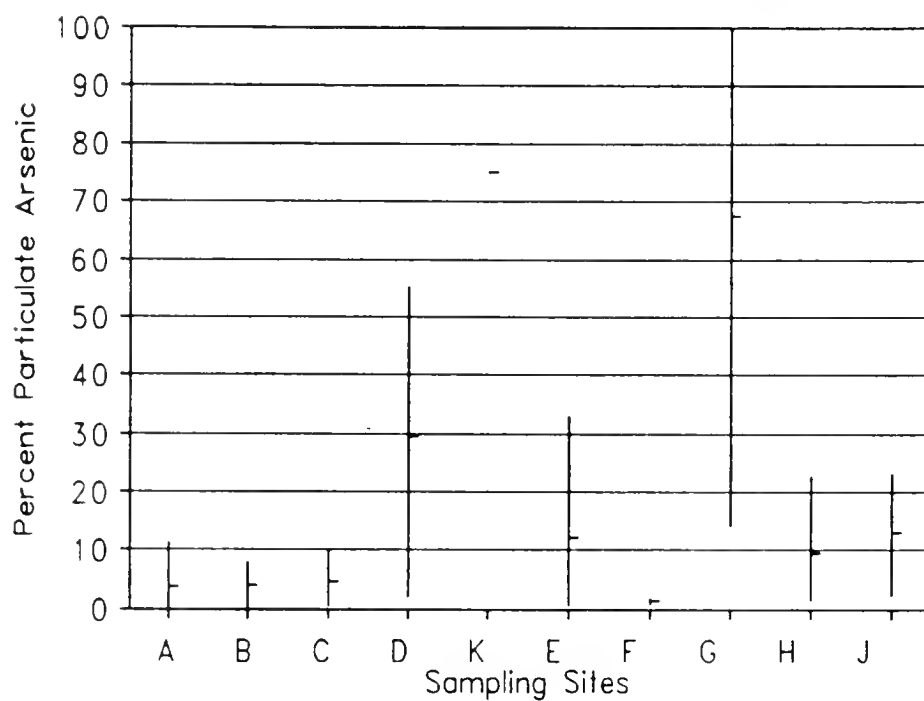
for mass of arsenic for sample run = mass of arsenic at Ennis
 $Y=0.9961X+8.28$ $R^2=0.758$

by the total arsenic concentration to yield the percentage of particulate phase arsenic. For the six samples from each complete sampling run, Figure 18 shows the range and mean percentage of particulate phase arsenic for each site.

The site showing the least variance in percentage of particulate arsenic (and the lowest mean) was Canyon Ferry. The sampling site at Canyon Ferry was on the power plant side of the dam; the inlet for the power plant is at the base of the dam, where a higher percentage of particulates might be expected. The spillway for the dam, which passes water over the top, was on the opposite side of the river. The chosen sampling site should have maximized the percentage of particulate arsenic in the sample.

In contrast to the Canyon Ferry site, the Toston site showed a greater range and higher mean percentage of particulate arsenic. These differences are not statistically significant above a 90 % confidence level. Table 12 organizes the data by stream discharge at each site. For Toston, the highest percentage was more than 32 times greater than the lowest percentage, while stream discharge varied by a factor of 14. At Canyon Ferry the percentage of particulate varied by less than one percent, while the stream flow varied by a factor of 1.7. These results demonstrate the moderating effect of Canyon Ferry in these two regards.

Figure 18
Percent Particulate Arsenic by Site



A. Ennis B. Black's Ford C. Madison River at Highway 10
 D. Jefferson River K. Gallatin River E. Toston
 F. Canyon Ferry G. Sun River H. Missouri River at Ulm
 J. Morony Dam

(Only one sample taken from the Gallatin River.)

Table 12 -Percent Particulate Arsenic by Site

Sample	Date	Flow (cfs)	Site	Percent Particulate Arsenic
A-1	05/09	1090	Ennis	1.22
A-6	08/29	1560		0.40
A-2	05/23	1610		5.15
A-4	06/17	2510		2.15
A-5	06/24	2630		1.68
A-3	06/06	6680		<u>11.42</u>
Average				3.7
C-1	05/09	1090	Madison @ Hwy 10	9.80
C-6	08/29	1560		0.52
C-2	05/23	1610		6.05
C-4	06/18	2510		3.43
C-5	06/24	2630		1.30
C-3	06/07	6680		<u>7.17</u>
Average				4.7
E-6	08/30	1510	Toston	0.55
E-1	05/10	4140		8.51
E-5	06/25	7870		3.89
E-4	06/18	9740		1.86
E-2	05/23	11300		25.98
E-3	06/07	21500		<u>32.88</u>
Average				12.3
F-1	05/14	4320	Canyon Ferry Reservoir	1.12
F-6	08/30	4350		1.61
F-2	05/24	4380		0.85
F-4	06/18	5830		1.80
F-5	06/25	6690		1.16
F-3	06/07	7370		<u>1.73</u>
Average				1.4
G-6	08/31	4650	Missouri @ Ulm	1.36
H-4	06/20	6980		4.75
H-1	05/15	7130		20.34
H-2	05/28	7780		22.75
H-5	06/26	8520		2.74
H-3	06/10	11200		<u>3.58</u>
Average				9.3
J-6	08/31	5500	Morony Dam	2.21
J-4	06/20	9330		6.01
J-2	05/28	12800		14.37
J-1	05/15	13000		23.26
J-5	06/26	13100		15.04
J-3	06/10	17400		<u>17.88</u>
Average				13.1

The higher mean percentage of particulate arsenic at Toston sets the stage for sedimentation in Canyon Ferry. One explanation for the increase in particulate phase arsenic between the Madison at Highway 10 and the Missouri at Toston can be inferred from a comparison of the sites on the Madison and Missouri rivers with the sites on their tributaries, the Gallatin, Jefferson and Sun rivers. Figure 18 shows the percentage of arsenic in the particulate phase in these tributaries far exceeds that found in the main river. It must be kept in mind, however, that these percentages are based on low- to detection-level concentrations of arsenic in the tributaries. The importance of these figures is not that they represent any substantial input of particulate phase arsenic per se, but that they may indicate an input of the components necessary to convert dissolved phase arsenic to the particulate phase. The geology of the area, as discussed in the introduction, supports the theory that clays would be more available below Cottonwood Creek on the Gallatin River and Sixteenmile Creek on the Missouri River.

Redox Aspects

Out of 55 samples analyzed for As(III) and As(V), all but two for As(III) were at or below the detection limit of four micrograms per liter. The other two samples were reported to contain eight micrograms per liter of As(III), which is within the lab's margin for error with this test. Although the reported As(V) concentration is not a perfect

match for the balance of the dissolved arsenic, it is still evident that the fully oxidized arsenate species dominate this system, and that the percentage of less oxidized arsenite species is negligible.

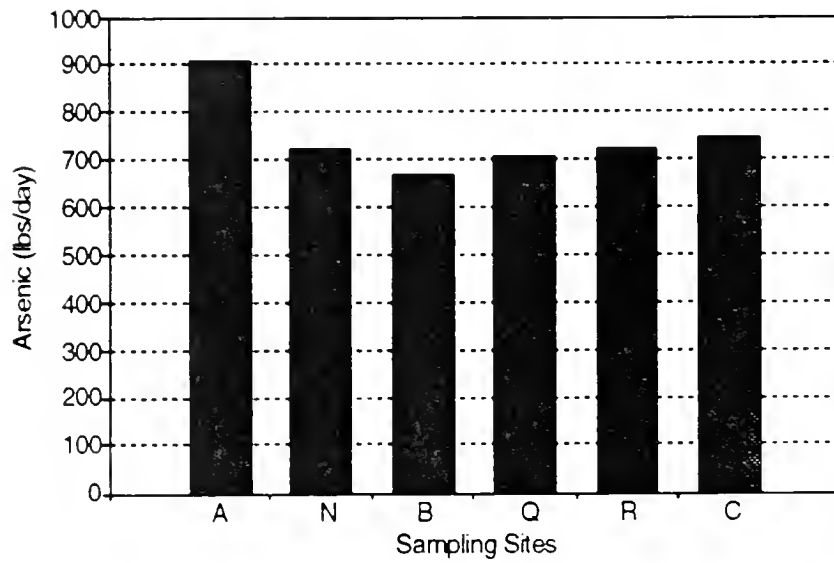
The primary significance of this relates to arsenic's availability to partition to the solid phase. Arsenate adsorbs and coprecipitates more readily than arsenite.

Black's Ford

The site at Black's Ford has been used in other studies and was a U.S.G.S. gaging station in the past. Figure 19 summarizes an additional sampling run of six sites from Ennis to Highway 10. Each bar represents one sample. There is no readily apparent reason why the arsenic flux should be so much lower at the Black's Ford site than it is below Ennis Dam. One possibility is that Cherry Creek, which enters the Madison 2.3 miles above Black's Ford, is not mixing completely with the river within this distance. Perhaps construction of a new bridge upstream has altered the channel.

The apparent drop in mass flux between the town of Ennis and Highway 10 requires explanation as well. Part of this drop may be accounted for by sedimentation in Ennis Lake. But, as described in the literature review (Sonderegger et al., 1989), in the twenty miles between Black's Ford and Highway 10 a substantial amount of water is removed from

Figure 19
Mass Flux Arsenic, Ennis to Three Forks



A. Ennis N. Below Ennis Dam B. Black's Ford
Q. Greycliff R. Cobblestone C. Madison at Highway 10

each bar represents a single sample taken 9/10/91

the river for agricultural irrigation. Some of this irrigation water is returned through surface returns and through groundwater movement, both of which are seasonal in nature and difficult to measure. At the same time, additions of water from tributaries like Cherry, Hot Springs, Bear Trap and Elk Creeks have a diluting effect. Since the nearest gaging station is Ennis Dam, these dilutions and removals are not easily accounted for by this study.

Conclusion

This thesis supports the following theories about the behavior of arsenic in the Madison and Missouri rivers:

1. With the possible exception of Canyon Ferry Reservoir, the behavior of arsenic in the study area during normal flow regimes is essentially conservative, moving through the river system quickly, in a predominantly dissolved, fully oxidized, state.

2. With the possible exception of Canyon Ferry Reservoir, little, if any, sedimentation of arsenic is occurring in the study area. This may be because of the limited availability of clays and iron, and, in the Madison, the relatively high velocity of the river.

3. The drop in the percent of particulate phase arsenic from the Toston site to the Canyon Ferry outlet suggests that sedimentation may be occurring in the reservoir. Although the data were not statistically significant above a ninety percent confidence level, it is an important enough aspect to warrant additional study.

4. The lack of arsenic(III) species at the Canyon Ferry outlet suggests that arsenic is not being released from the sediments through anaerobic reduction. However, the evidence may be the result of flow regimes within the reservoir which were specific to the period of study, seasonally or hydrologically. If arsenic ordinarily accumulates in the

sediments, but is released back into the water column during occasional episodes of anaerobic sediment conditions, those episodes have the potential to be catastrophic.

Recommendations

This thesis has raised many questions, which warrant further investigation. Several of them follow.

- a) What is the arsenic content in the sediments, particularly in the reservoirs? Is particulate arsenic accumulating, and is it adsorbed or chemically bound (what conditions would be required to free the arsenic)?
- b) What are the flow regimes, seasonal or otherwise, which occur in Canyon Ferry Reservoir?
- c) Are the reservoir's sediments aerobic, anaerobic or seasonally variable? How are they affected by hydrologic variables, such as annual precipitation and snow melt?
- d) What are the interactions between the reservoir and the local groundwater, and is the groundwater being contaminated by arsenic from the reservoir?
- e) How constant are the primary sources, and what factors control them?

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Appendices

Appendix A
Hydrology data by river mile

River Mile	Eleva- tion (feet)	Add Drain- age Area (sq mi)	Total Drain- age Area (sq mi)	Site	USGS Station #
133	6650		420	West Yellowstone	06037500
122	6535			Hebgen Lake	
109	6535		904	Hebgen Lake	6038000
108	6448		905	Hebgen Dam	6038500
107	6400	31.5		cnf Cabin Cr.	
106	6388				
105	6388	44.5		cnf Beaver Cr.	
102	6388			Quake Lake	
101	6360				
100	6200	10.5		cnf Sheep Cr.	
99	6160				
98	6120				
97	6080	22		cnf Mile Cr.	
96	6040				
95	6000				
92	5960				
90	5880		1065	Kirby Ranch	06038800
89		231		cnf W Fork Madison,	Papoose Cr.
88	5820	18.3		cnf Squaw Creek	
87	5800	25.5		cnf Standard Cr.	
86	5760				
85		28		cnf Horse Cr.	
84		17.5		cnf Moose Cr.	
79	5600				
78	5560				
76	5520				
75	5500	41.5		cnf Ruby Cr.	
73	5480				
72		38		cnf Corral Cr.	
71	5400	99		cnf Indian Cr.	
69	5360				
65	5300	22		cnf Morgan Gulch	
64	5260				
62	5200				
61	5180				
56	5060				
55	5040	59.5		cnf Blain Spring Cr.	
53	5000				
51				Ennis	
49	4900	137		cnf O'Dell Cr.	
47	4860	51.5		cnf Jack Cr.	
46		41		cnf Moore Cr.	
44	4841.5	29.5		cnf Spring Cr.	
43		77		cnf Meadow Cr.	
42		18.5		cnf Jourdain Cr.	

River Mile	Eleva- tion (feet)	Add Drain- age Area (sq mi)	Total Drain- age Area (sq mi)	Site	USGS Station #
40	4841.5		2181	Ennis Lake	
39	4689		2186	Below Ennis Dam	06041000
37	4640				
36	4600	14.5		cnf Bear Trap Cr	
33	4560				
31	4520	72.5		cnf Hot Springs Cr.	
29	4480				
28			2288	Bear Trap cmpgrnd	
27	4440				
26		45.5		cnf Cherry Creek	
25	4410				
24	4400		2387	Black's Ford	
23	4390	46		cnf Elk Cr.	
19	4320				
18	4290			Greycliff	
17	4265				
16	4250				
15	4235				
14	4210				
12	4180			Cobblestone	
11	4165				
10	4150				
8	4130				
7	4095				
5	4080				
3	4060		2511	Madison @ Hwy 10	06042500
2	4050				
0	4040	9532		cnf Jefferson R.	
-1		1795		cnf Gallatin R.	
-2	4030				
-3	4020				
-7	4000				
-16	3960				
-17		516		cnf Sixteen Mile Cr.	
-23	3920				
-25	3906		14669	Toston Station	6054500
-26	3900				
-28		65		cnf Six Mile Cr.	
-30	3880	157		cnf Crow Cr.	
-32	3870				
-34	3860	65		cnf Dry Cr.	
-36		40		cnf Greyson Cr.	
-37	3840				
-38	3820	111		cnf Deep Cr.	
-42		51		cnf Indian Cr.	
-43	3800				
-44	3797	32		cnf Cottonwood Cr.	
-45	3797				
-46	3797				

River Mile	Eleva- tion (feet)	Add Drain- age Area (sq mi)	Total Drain- age Area (sq mi)	Site	USGS Station #
-47	3797	40		Ray Cr.	
-48	3797	31		cnf White Horse Cr.	
-49	3797	17		cnf Dry Gulch	
-50	3797	25		cnf Gurnett Cr.	
-51	3797	30		cnf Duck Cr.	
-52	3797				
-53	3797	74		cnf Confederate Gulch	
-56	3797	86		cnf Beaver Cr.	
-58	3797	45		cnf White Cr.	
-60	3797	9		cnf Bilk Cr.	
-62	3797	42		cnf Avalanche Cr.	
-64	3797	20		cnf Hellgate Gulch	
-66	3797	33		cnf Magpie Cr.	
-68	3797		15904	Canyon Ferry Dam	06058500
-69	3650			Hauser Lake	
-70	3646				
-72	3646	46		cnf Spokane Cr.	
-76	3646	77		cnf Trout Cr.	
-78	3646	39		cnf Soup Cr.	
-82	3646	610		cnf Prickley Pear Cr.	
-84	3646		16876	Hauser Dam	
-85	3578	77		cnf Beaver Cr.	
-86	3578			Holter Lake	
-89	3578	53		cnf Towhead Gulch	
-100	3578	21		cnf Cottonwood Cr.	
-110	3578		17149	Holter Dam	60606500
-111	3464				
-113	3460	381		cnf Little Prickley Pear Cr.	
-114		35		cnf Rock Cr.	
-117			17739	Craig	
-118	3440	30		cnf Wegner Cr.	
-120		49		cnf Stickney Cr.	
-123		325		cnf Dearborn River	
-129	3400				
-134	3380	39		cnf Sheep Cr.	
-135		17		cnf Hardy, Prewett Crs.	
-136	3360				
-145			18493	Cascade	
-147	3340				
-153		62		cnf Bird Cr.	
-155		244		cnf Little Muddy Cr.	
-156	3335				
-170		30		Ulm Coulee	
-171	3325	2006		cnf Smith River	6078000
-180	3321		20941	Ulm Gaging Station	6078200
-182	3319				
-186	3317				
-191	3315				
-193	3314				

River Mile	Eleva- tion (feet)	Add Drain- age Area (sq mi)	Total Drain- age Area (sq mi)	Site	USGS Station #
-195		190		cnf Sand Coulee Cr.	
-199	3312	1937		cnf Sun River	
-203	3310		23124	Black Eagle Dam	
-204	3240				
-206	3240			Rainbow Dam	
-207	3200				
-209	3126			Cochrane Dam	
-210	3050				
-211	3050			Ryan Dam	
-213	2900	96		cnf Box Elder Cr.	
-214	2900			Morony Dam	
-215	2807		23292	Gaging Station	06090300

Appendix B

Arsenic Study Data- by Site

Sample	Date	Start Time	Temp. (C)	pH	Spec Cond (uS/cm)	Alkalinity (as mg/l CaCO3)	Total Unfiltered Arsenic (ug/l)	Total Dissolved Arsenic (ug/l)	+3 (ug/l)	+5 (ug/l)	Total Sediment Arsenic (ug/l)	Flow (cfs)	Site	NOTES
A-1	05/09	10:00	6.9	7.90	0.331	103	113	116	4	108	1.43	1090	Ennis	
A-2	05/23	9:00	9.1	8.23	0.290	99	99	95	<4	88	5.16	1610	Ennis	
A-3	06/06	15:00	10.9	8.18	0.221	84	60				7.21	6680	Ennis	21
A-4	06/17	15:15	14.1	8.37	0.219	75	61	59	8	48	1.30	2510	Ennis	131
A-5	06/24	13:00	13.7	8.58	0.220	75	63	64	<4	52	1.09	2630	Ennis	161
A-6	08/29	8:50	12.9	8.19	0.268	92	86	86	<4	64	0.35	1560	Ennis	
A-7	09/10	8:40	11.6	8.22	0.268	91	90	94	<4	80		1870	Ennis	
B-1	05/09	12:30	7.5	8.45	0.303	117	6	8	<4	<4	1.97	1090	Bear Trap	111
B-2	05/23	11:00	10.5	7.92	0.124	69	19	18	<4	16	1.54	1610	Black's Ford	
B-3	06/06	17:00	13.3	8.08	0.176	68	38				2.68	6680	Black's Ford	
B-4	06/17	17:45	14.8	8.59	0.177	65	40	41	4	36	1.00	2510	Black's Ford	
B-5	06/24	15:30	16.3	8.71	0.189	69	48	50	<4	44	1.66	2630	Black's Ford	161
B-6	08/29	11:00	18.1	8.93	0.274	107	80	79	<4	77	0.33	1560	Black's Ford	
B-7	09/10	12:00	16.7	9.07	0.278	104	66	62	<4	60		1870	Black's Ford	

Sample	Date	Start Time	Temp (C)	pH	Spec Cond (uS/cm)	Alkalinity (as mg/l CaCO3)	Total Unfiltered Arsenic (ug/l)	Total Dissolved Arsenic (ug/l)	+3 (ug/l)	+5 (ug/l)	Total Sediment Arsenic (ug/l)	Flow (cfs)	Site	(NOTES)
C-1	05/09	17:30	8.3	8.41	0.328	114	75	75	<4	60	8.15	1090	Madison @ Hwy 10	
C-2	05/23	13:45	16.8	8.30	0.267	125	70	59	<4	60	3.80	1610	Madison @ Hwy 10	
C-3	06/07	7:30	13.7	7.94	0.231	82	62				4.68	6680	Madison @ Hwy 10	
C-4	06/18	7:15	11.4	8.06	0.226	83	61	59	<4	52	2.10	2510	Madison @ Hwy 10	(6)
C-5	06/24	17:30	18.7	8.66	0.230	88	66	69	<4	56	0.91	2630	Madison @ Hwy 10	(6)
C-6	08/29	13:50	19.3	8.64	0.290	109	90	91	<4	84	0.48	1560	Madison @ Hwy 10	
C-7	09/10	17:20	19.1	9.27	0.283	105	74	82	<4	65		1870	Madison @ Hwy 10	
C-8	09/19	11:30	11.7	8.49	0.287	109	60	74	<4	62	0.34	1630	Madison @ Hwy 10	
C-9	09/19	12:40	12.4	8.60	0.287	111	62	79	<4	64	0.33	1630	Madison @ Hwy 10	
C-10	09/19	13:35	13.4	8.80	0.286	102	62	78	8	64	0.38	1630	Madison @ Hwy 10	
D-1	05/10	13:00	9.2	8.37	0.346	122	3	3	<4	4	0.77	1570	Jefferson	
D-2	05/23	15:30	17.7	7.95	0.190	101	8	6	<4	8	3.01	4350	Jefferson	
D-3	06/07	9:30	13.9	7.70	0.200	78	9				5.23	8040	Jefferson	
D-4	06/18	9:05	13.9	7.92	0.214	88	6	3	<4	8	1.67	4410	Jefferson	(6)
D-5	06/25	7:00	14.5	8.15	0.246	96	4	4	<4	8	1.68	3410	Jefferson	(6)
D-6	08/29	15:15	21.8	8.79	0.494	171	3	4	<4	<4	0.08	180	Jefferson	
E-1	05/10	15:30	9.0	8.22	0.341	132	23	21	<4	16	1.95	4140	Toston	
E-2	05/23	17:30	15.3	7.93	0.221	104	15	11	<4	16	3.86	11300	Toston	
E-3	06/07	11:45	13.1	7.89	0.207	79	21				7.27	21500	Toston	
E-4	06/18	11:30	14.5	8.07	0.225	86	18	17	<4	16	0.32	9740	Toston	(2, 4, 6)

Sample	Date	Start Time	Temp. (C)	pH	Spec Cond (uS/cm)	Alkalinity (as mg/l CaCO3)	Total Unfiltered Arsenic (ug/l)	Total Dissolved Arsenic (ug/l)	+3 (ug/l)	+5 (ug/l)	Total Sediment Arsenic (ug/l)	Flow (cfs)	Site	NOTES
E-5	06/25	9:30	15.8	8.25	0.240	98	23	16	4	16	1.52	7870	Toston	(3)
E-6	08/30	12:35	20.7	8.97	0.341	139	62	59	<4	60	0.33	1510	Toston	(6)
K-6	08/30	12:35	20.7	8.97	0.341	139	60	57	<4	48	0.35	1510	Toston (duplicate)	
F-1	05/14	13:00	5.5	8.56	0.385	149	30	31	<4	16	0.35	4320	Canyon Ferry	
F-2	05/24	9:00	7.1	8.61	0.388	159	26	25	<4	28	0.22	4380	Canyon Ferry	
F-3	06/07	14:30	8.5	8.71	0.382	142	30				0.55	7370	Canyon Ferry	(1)
F-4	06/18	17:40	10.3	8.58	0.376	146	28	28	<4	28	0.51	5830	Canyon Ferry	(2, 6)
F-5	06/25	12:15	10.3	8.44	0.375	143	28	31	4	24		6690	Canyon Ferry	(3)
F-6	08/30	16:00	15.8	7.78	0.323	131	23	30	<4	28	0.35	4350	Canyon Ferry	(1, 6)
G-1	05/15	11:30	11.8	8.28	0.358	164	1	1	<4	<4	3.62	2540	Sun River @ G.F.	(5, 7)
G-2	05/28	9:30	11.0	8.30	0.309	127	2	2	<4	8	3.91	4350	Sun River @ G.F.	
G-3	06/10	11:30	13.3	8.16	0.292	145	2				2.61	5320	Sun River @ G.F.	
G-4	06/20	13:30	14.3	8.20	0.452	160	1	1	<4	4	2.26	1800	Sun River @ G.F.	(5, 6)
G-5	06/26	7:00	12.5	8.21	0.348	145	1	1	<4	<4	3.43	4650	Sun River @ G.F.	(5, 6)
H-6	08/31	12:40	20.4	8.54	0.556	209	1	2	<4	<4	0.33	614	Sun River @ G.F.	

Sample	Date	Start Time	Temp. (C)	Spec Cond (uS/cm)	Alka- linity (as mg/l CaCO3)	Total Unfiltered Arsenic (ug/l)	Total Dissolved Arsenic (ug/l)	+3 (ug/l)	+5 (ug/l)	Total Sediment Arsenic (ug/l)	Flow (cfs)	Site	(NOTES)
H-1	05/15	9:30	11.7	8.44	0.315	135	13	15	<4	12	3.83	Missouri @ G.F.	
H-2	05/28	13:00	8.8	8.12	0.291	139	17	14	<4	20	4.12	Missouri @ G.F.	
H-3	06/10	9:30	13.9	8.31	0.350	147	20	22	<4	24	0.75	Missouri @ G.F.	
H-4	06/20	11:00	14.4	8.43	0.360	148	22	22	<4	20	1.10	Missouri @ G.F.	(6)
H-5	06/26	9:00	14.5	8.38	0.367	161	19	22	<4	20	0.62	Missouri @ G.F.	(1, 6)
G-6	08/31	10:00	20.3	8.69	0.358	138	25	25	<4	28	0.35	Missouri @ G.F.	
J-1	05/15	14:00	12.5	8.32	0.348	148	10	10	<4	<4	3.03	Morony Dam	
J-2	05/28	16:00	11.3	8.22	0.309	129	9	8	<4	12	1.34	Morony Dam	
J-3	06/10	14:30	14.5	8.42	0.338	127	12			2.26	17400	Morony Dam	
J-4	06/20	16:00	15.1	8.36	0.360	138	18	18	<4	16	1.15	Morony Dam	(6)
J-5	06/26	11:30	14.4	8.40	0.365	159	11	12	<4	12	2.12	Morony Dam	(6)
J-6	08/31	14:35	19.8	8.46	0.408	152	18	17	<4	20	0.38	Morony Dam	
K-1	05/09	15:00	8.5	8.25	0.330	158	2	2	<4	<4	6.04	Gallatin	
N-7	09/10	10:00	15.9	8.80	0.286	100	72	75	<4	68	1870	Below Ennis Dam	
Q-7	09/10	13:20	17.9	9.16	0.279	98	70	75	<4	62	1870	Greycliff	
R-7	09/10	14:35	18.5	9.14	0.281	101	72	76	<4	66	1870	Cobblestone	
S-7	09/10	16:15	18.2	8.81	0.497	216	69	67	<4	62		Irrigation Return	

- (1) Actual value of the sediment is . 2.5 ug which is the detection limit.
Concentration value for the sediment should also be read as "less than"
the given value.
- (2) Total dissolved arsenic value and speciation performed on sample preserved with HNO₃
- (3) Total dissolved arsenic value and speciation performed on sample preserved with HCl
- (4) Top sediment value is for coarse fraction (45 um< S <63 um) Sediment value on second line is fine fraction (<45 um)
- (5) Actual value of total dissolved arsenic is <1 ug/L which is the detection limit.
- (6) Due to the use of a dilution process the detection limit on the speciations was 4 ug/L
- (7) Actual value of total unfiltered arsenic is <1 ug/L which is the detection limit.

Flow data for sites from Ennis to the Madison at Highway 10, inclusive,
is from Ennis dam, which is the nearest working gaging station

This thesis has been examined and approved for acceptance by the Department of Environmental Engineering, Montana College of Mineral Science and Technology, on this 8TH day of August, 1992.

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